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ABSTRACT

This publication is a handbook used in conjunction with the course of study in chemistry developed through the New York State Education Department and The University of the State of New York. It contains experiments, demonstrations, and other activities for a chemistry course. Areas covered include the science of chemistry, the atomic structure of matter, solutions, metals and metallurgy, non-metals, ionization, acids, bases and salts, organic chemistry, nuclear energy, and reaction principles. Suggestions are included in the appendices relating to visual aids, planning field trips, preparing reports, suggested readings and facts related to equipment and supplies. General references and bibliographical data are included. (EB)

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CHEMISTRY

A Handbook of Activities to Accompany the Course of Study in Chemistry

The University of The State of New York
The State Education Department
Bureau of Secondary Curriculum Development

2

CHEMISTRY

Experiments, Demonstrations and Other Activities Suggested for Chemistry

The University of The State of New York
The State Education Department
Bureau of Secondary Curriculum Development

Reprinted 1975

THE UNIVERSITY OF THE STATE OF NEW YORK

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Foreword

This handbook has been designed to accompany the chemistry syllabus which was revised and distributed in 1957. It is hoped that this handbook will serve both new and experienced teachers. Effective and timesaving suggestions are given for improving teaching through the inclusion of demonstrations and laboratory work. All teachers will find use for the suggestions for varied instructional techniques not readily available elsewhere. Background information on relatively "new" aspects of chemistry, possible pupil projects, bibliographies and other sources of reference materials should prove helpful. Emphasis has been placed upon those safety aspects peculiar to the chemistry classroom and laboratory.

In using the handbook it is expected that the teacher will discriminate in the selection of activities, depending upon the nature of the class, the materials available and personal experience. Whenever a teacher has students of exceptional promise in science, whether an individual or group, wider horizons of instruction should prevail. To assist the teacher in this situation liberal references indicating advanced materials have been included at the end of most areas. Considerable helpful materials will be found in the appendixes.

Some of the material used in this handbook was contributed originally by Reverend Laurence J. McGowan, Archbishop Stepinac High School, White Plains; Rolland J. Gladieux, director of mathematics and science, Kenmore; Raymond Byrne, Batavia High School; and Samuel Bloom, Benjamin Franklin High School, Rochester. Elizabeth V. Lamphere, chairman, science department, Norwich City Central Schools; and Fred Riebesell, associate professor, State University College at Oneonta, prepared considerable new materials and activities and reworked some of the earlier contributions. Numerous teachers throughout the State offered additional assistance. Herbert A. Steinke, formerly supervisor of art in the Albany public schools, prepared the illustrations.

Hugh B. Templeton, supervisor of science education, acted as consultant during the organization of the project. Robert G. MacGregor, associate in science education, wrote extensive additional materials and revised much of the original material for the final draft. John V. Favitta, associate in science education, gave the manuscript a careful reading, offered valuable suggestions regarding changes, rewrote portions and provided additional diagrams. Herbert Bothamley, formerly associate in secondary curriculum, organized the final manuscript and edited it in preparation for publication.

Introduction

THE SCIENCE OF CHEMISTRY

It has been said that the beginning of applied chemistry occurred before the dawn of history. In that beginning, prehistoric men and women tamed fire, developed ceramics, discovered medicinal herbs and poisons, exploited the properties of natural cements and plastics, forged iron from meteorites and learned to reduce copper from its ores.

Chemistry as a pure science budded in the Old Kingdom of the Nile, when Egyptian priests began the process of seeking the interrelationships among the various kinds of material that make up the world. While man has lived to see this task largely accomplished, new questions and new unknowns have been raised in the process. Medieval alchemists delivered into the hands of early modern scientists of the 16th century a number of known elements and compounds such as sulfuric, hydrochloric and nitric acids, alkalis, salts and organics. Firmly established chemical industries of this period included: metallurgy, dyeing, tanning, ceramics, papermaking, glassmaking and explosives. Each new generation of chemists has provided for the needs, resources, health, luxuries, food, safety and defense for millions of peoples.

Out of centuries of human labor has grown a sound, complex, vital discipline known as the science of chemistry. It stands across both time and continents as one of the greatest intellectual and practical achievements of man. It is a major branch of scholarship which lies at the root of all medical advance. It holds the solutions to problems of world food and fuel supplies, economic health, political stability, national defense and man's ceaseless hunger to understand the universe. The teacher of chemistry should properly feel the majesty of this saga and exhibit pride at these great accomplishments for the human race.

THE CHEMISTRY COURSE

The aims and objectives of a chemistry course should reach far beyond the mere assimilation of factual chemical knowledge. The chemistry course should be a practice laboratory in which the "scientific method" is really appreciated and attitudes of true experimentation are developed. The creativity necessary for bringing about new discoveries is to be fostered together with the realization that the worlds of today and tomorrow depend upon these new discoveries for their success.

It is important to stress the role of chemistry in economics and its possible utilization in the future careers of the pupils. Appreciation of the benefits to citizens which constantly flow from the workshops of chemistry for health, security, productivity and peace should be made an inherent part of the objectives.

The chemistry syllabus has been designed as a practical solution to the real class problem where terminal pupils, college preparatory students and future scientists may be taught in one group. It provides a respectable standard of scientific content for the student who intends to major in science without necessarily eliminating a terminal pupil of average ability. Emphasis has been shifted away from descriptive content somewhat, toward the understanding of principles and concepts. This does not mean to imply that descriptive chemistry and the mastery of fundamental subject content have become lesser in importance, but rather that these areas contain the type of material best suited to the election of the individual teacher. The syllabus and handbook may be used together most effectively: the syllabus as a flexible course outline and the handbook as a source of interesting activities from which the teacher may select suggestions to substantiate the listings found in the syllabus.

Regents examinations will be based in part upon activities found in this handbook. Care will be taken to construct questions in such a manner as to test facts and principles. It will not be necessary for any individual pupil to have performed all the activities.

SCHEDULING THE CHEMISTRY COURSE

The minimum time recommended for the study of chemistry is six 45-minute periods a week. When six periods a week are scheduled it is desirable to have a double laboratory period to provide time for certain types of laboratory exercises and/or short field trips.

To achieve the maximum benefits of the science laboratory the teacher must give individual attention to situations as they arise. Pupil-teacher contacts, remedial opportunities and effective supervision decline sharply with increased size of classes. It is recommended that the chemistry recitation class not exceed 24 pupils and that the laboratory class not exceed 16.

ADVANCED PLACEMENT COURSES IN CHEMISTRY

Where adequate teaching skill, equipment and time are available, schools may wish to consider providing advanced placement courses in chemistry for students who possess the ability and drive to accomplish college-level work during their 12th year. The College Entrance Examination Board offers a special examination for such students each May. Upon receipt of the results colleges, at their own discretion, may award to the student exemption from all or part of the first-year chemistry course. Some students may thus gain an entire year of time in their professional training. The abilities of the school, the teacher and the students should be carefully weighed before devoting time to the development of such a program.

The Bureau of Secondary Curriculum Development has prepared the publication *Advanced Placement Program in Chemistry*. This bulletin offers guides to high school administrators and teachers for developing college-level courses in chemistry.

THE CHEMISTRY LABORATORY PROGRAM

The teacher is responsible for the effectiveness of the laboratory program. Pupils *must* understand the purpose of the laboratory work and the necessity for using accepted techniques in performing the activities which are chosen. The proper appreciation, by the pupils, of the scientific method will largely depend upon the degree to which the teacher develops a sequential and meaningful laboratory program.

Laboratory exercises should be performed individually or in small groups. Demonstrations involving as much pupil participation as possible should be performed frequently by the teacher as one of a variety of instructional techniques. However, such demonstrations cannot be considered a substitute for pupil-performed exercises because they do not provide for manipulation of materials, observation, and the correction and interpretation of data by each individual pupil. Students of superior ability who have a keen interest in chemistry can profit greatly from project work and may even carry on some actual original research when facilities and supervision are available.

Laboratory Requirements

One of the requirements for the successful completion of the chemistry course on a full-time basis is that the pupil shall have spent at least 30 periods in the laboratory performing laboratory work and shall have prepared a written record of this work in a notebook. Most pupils should complete a minimum of approximately 30 exercises. However, the number of exercises that should be performed depends upon the type selected. Notebooks should be retained by the school for at least six months after the final examination.

It is difficult to justify the practice of requiring exercises in which all observations and conclusions can be recorded by reading a textbook or workbook rather than by actually performing the exercise. An extremely important outcome of laboratory work is the ability to record data and write reports in an accurate and concise manner. It is suggested that teachers be as critical of spelling, grammatical errors and clarity of the reports as they are of laboratory techniques.

Laboratory Techniques

The development of certain techniques for the *safe* handling of chemicals and apparatus is a major objective of laboratory work. College students and those in training as nurses and laboratory technicians have frequently reported that their inexperience in assembling apparatus in the high school chemistry laboratory has hindered their progress in advanced science courses. Although it is desirable that superior students engage in some research projects requiring several periods for completion, such assignments should be made only after these students have acquired these basic skills in handling apparatus.

The workbook-cookbook approach to laboratory experience may be tolerable during the first few weeks of the course when the pupils are learning how to handle apparatus. Beyond this point a more truly experimental operation is suggested. Some ways to provide for this effective form of experimentation include:

- Plan laboratory experiences before the class discussion, thus putting observations in their proper relation to conclusions.
- Conceal the expected outcome of the experiment as often as possible.
- Require the pupils to design some exercises themselves beginning with simpler steps. Toward the end of the course, they should be expected to design the whole procedure.
- Have each pupil work with a different amount of material when the exercise can be made quantitative; for example, solubility curves and percentage composition.
- Use "unknowns" after first working with "knowns."
- Assign a different method to each group of pupils in situations where there are alternate methods for preparing compounds.
- Use the semimicro technique for pupils at either end of the ability spectrum since this technique allows each to progress at his own rate.

Semimicro Technique

The use of semimicro equipment in the high school chemistry laboratory, although a relatively new technique, is increasing. One of the principal differences between the usual high school laboratory equipment and its semimicro counterpart is the size. For many pieces of equipment, the essential difference between macro and semimicro equipment is the smaller size of the semimicro equipment.

While an Erlenmeyer flask commonly used in macro work has a capacity of about 250 ml., an Erlenmeyer flask in semimicro work has a capacity of about 50 ml. A common macro test tube might have a capacity of about 15 to 20 ml. while a semimicro test tube commonly has a capacity of 3 to 5 ml.

In addition to flasks and test tubes this is also true, for example, of such items as beakers, funnels, crucibles, mortar and pestles, watch glasses, thistle tubes, gas collecting bottles and bunsen burners.

Aside from size, however, semimicro differs from macro work in other ways. Most of the required chemicals in macro work, for example, are usually provided for the pupils at the time they are needed for a specific experiment. In semimicro work, by contrast, pupils are provided with a kit or tray of most of the chemicals that are needed for the entire laboratory work of the year. If necessary, more than one class may use the same kits. Kept in wooden trays, highly concentrated solutions of the common acids and bases are also provided pupils in semimicro work. Pupils prepare more dilute solutions of these acids and bases as they are needed.

Many reactions are effected by adding reagents dropwise to glass microscope slides that are considered to be another essential part of semimicro equipment. Some reactions, too, are effected in specially designed tapered test tubes (centrifuge tubes) so that small amounts of precipitate may be separated more easily and quickly from solutions by decanting. Centrifuges are, therefore, necessary pieces of equipment in semimicro work–about four centrifuges per class of 16 pupils. The processes of centrifuging and decanting frequently replace the macro process of filtering which is usually too slow a process for many semimicro operations.

While weighing chemicals roughly to the nearest tenth of a gram is sufficient in most macro operations, weighing to the nearest hundredth of a gram is commonly desirable and necessary in semimicro work. At least six of these balances per class of 16 pupils are recommended.

Before attempting the use of semimicro equipment the teacher should realize that a greater degree of coordination on the part of pupils is needed and that supervision becomes more limited.

The use of semimicro equipment (all or in part) satisfies all laboratory requirements.

Pretesting Demonstrations and Laboratory Exercises

The teacher is strongly urged to pretest all demonstrations and laboratory exercises. An unrehearsed demonstration or exercise is likely to create the same audience impression as an unrehearsed play.

POSSIBLE TEACHING SEQUENCES

The chemistry syllabus, as outlined in *Chemistry and Physics,* cannot be considered in its entirety as a teaching sequence. Several sequences are not only possible but have been successfully used. Teachers of any chemistry course usually find that they must present several topics up to a certain point and then retrace their steps to fill in the gaps. They often feel that a certain given topic cannot be presented until all other topics have been taught. The necessity for this method of presentation makes it difficult to prepare a brief teaching sequence. With the limitations described above, two possible sequences are suggested:

Teaching Sequence I

This sequence is suggested largely by the arrangement of topics in this handbook. Atomic structure and the periodic table are presented early in the course. Frequent references are made to the periodic table and to principles of reaction in explaining certain topics under metals and nonmetals. Mathematical applications are presented as needed and range from the simple minimum required problems to more advanced optional extensions which should challenge the more able students.

Teaching Sequence II

Sequence	*Syllabus Topics*
Introduction	1. *Looking at the Work of the Chemist*
Solutions and Water	2. *Solutions and Near Solutions*
Oxygen and Hydrogen	3. Nonmetals, III and IV
Atomic Structure	4. The Atomic Structure of Matter, I and II
Chemical Nomenclature, Formulas, Equations and Problems	5. *The Language and Mathematics of Chemistry*

Periodic Table, Metals, Nonmetals and Inert Elements	4. Atomic Structure, III 9. Metals, I; 3 Nonmetals, I and II
The Halogens and Their Compounds	3. Nonmetals, V
Sodium and Calcium Compounds	9. Metals, IV and V
Ionization	6. *Ionization, Acids, Bases and Salts*
Sulfur and Its Compounds	3. Nonmetals, VI
Nitrogen and Its Compounds	3. Nonmetals, VII and VIII
Carbon and Its Oxides	3. Nonmetals, IX
Nuclear Energy	7. *Nuclear Energy*
Organic Chemistry	8. *Organic Chemistry*
Metallurgy	9. Metals and Metallurgy, II and III
Principles of Reaction	10. *Principles of Reaction*

THE PLACE OF MATHEMATICS IN CHEMISTRY

The prerequisite for enrollment in the Regents course in chemistry is the successful completion of the course in ninth year mathematics—course 1 (algebra). Experience has shown that tenth year mathematics is also very desirable. It has also shown that grades of less than 80 percent in either of these mathematics courses are predictors of considerable difficulty in chemistry and physics.

In most cases in this handbook, required mathematical applications or suggested optional mathematical extensions have been included in connection with related activities. It is recommended that mathematics be introduced into the content wherever appropriate rather than concentrating this study into a short period of time.

Appendix *E* contains information dealing with significant figures and powers of 10, topics that are appropriate for pupils of above-average ability. While the use of the slide rule is not required, the development of this skill is very desirable, particularly for pupils who plan to take advanced science courses.

SPECIAL SAFETY PRECAUTIONS

Throughout this handbook strong emphasis has been placed upon safety precautions in the chemistry classroom and laboratory. School administrators may also wish to consider the following two recommendations in determining local school policy in regard to safety.

Protection for the Eyes

The excellent safety record in the chemical industry is due in part to the fact that all persons are required to wear glasses while in the laboratories. It may be desirable to require that teachers and pupils wear glasses, visors or similar protective devices when performing demonstrations and experiments. Such devices should be considered basic items of equipment.

Experimentations with Rockets and Rocket Fuels

Rocket research is being conducted by highly trained specialists working in isolated areas with the strictest safety precautions known. The handling of propellants involving chemical reactions requires a specialized training that few, *if any*, teachers and pupils possess. It is desirable to prohibit such experimentation as a school activity and to discourage it as nonschool activity. Upon request the specialists at nearby military installations may be willing to offer advice on the subject of explosives.

Survey of Safety Procedures

Appendix *A* is devoted entirely to safety recommendations for use in the chemistry laboratory.

The Science of Chemistry

1.01. Methods of Science

The scientist employs an orderly method of organized thinking to solve a problem objectively. This systematic approach is called the *scientific method.* Science may be described as "a series of concepts or conceptual schemes (theories) arising out of experimentation or observation and leading to new experiments and further observation." The test of a scientific theory should be its fruitfulness, its ability to suggest, its stimulation and its direction to further experimentation (see reference *1R-1*).

Science is an orderly process involving the formation of broad working hypotheses that may eventually become new theories. Through experimentation, there is a testing of deductions which leads to the accumulation of new data and perhaps to new hypotheses and further experimentation. By using a similar approach in the teaching of science, it is expected that the pupil can gain some comprehension and understanding of the methods of science (see reference *1R-2*).

a. Present to pupils a schematic approach to problem solving such as the following:

- Observation of phenomena
- Construction of hypothetical patterns (identification of a problem)
- Establishment of experimental facts
- Construction of satisfying patterns (theories) possible of independent verification
- Understanding → comprehension → prediction

b. Discuss with the pupils the manner in which scientists employ an orderly method of thinking (see reference *1R-3*):

- Problems → hypotheses → survey of literature → experimentation → controls → cause and effect → tentative conclusions → open-mindedness → application
- Limitations of the scientific method
- Application of the scientific method to fields other than science
- Search for the truth leads to the benefit of man

1.02. Identifying and Checking Equipment

a. Prepare a form similar to the one shown below and provide each pupil with his own copy. Use the overhead projector to identify the items of equipment and instruct pupils to "check off" each item in his desk when it is identified (see appendix *B-1*). See references *2R-4-5* for additional helpful hints in the use of the overhead projector.

PUPIL'S NAME____________________ DRAWER NUMBER________ DATE________

NAME OF SUPPLY OR APPARATUS	QUANTITY	CHECK ✓		REMARKS
		IDENTIFIED & RECEIVED	RETURNED	
Beaker, ____ ml., ____ ml.				
Bone or plastic spoon				
Bottles, wide mouth, ____ oz.				
Bunsen burner and hose				
Burette clamps				
Crucible and cover				
Deflagrating spoon				
Erlenmeyer or Florence flasks, ____ ml.				
Evaporating dish				
File, triangular or glass tubing cutter				
Filter paper				
Forceps				
Funnel				
Glass squares				
Graduate, ____ ml.				
Litmus paper, red and blue				
Medicine dropper				
Metric ruler				
Mortar and pestle				
Pinchcocks				
Pipestem triangle				
Pneumatic trough				
Ringstand and clamps				
Rubber or plastic connections				
Safety matches				
Sponge				

Stirring rod				
Stoppers, cork and rubber				
Test tube, pyrex ——— ml., ——— ml.				
Test tube brush				
Test tube holder				
Test tube rack				
Thistle tube				
Tongs				
Tripod				
Watchglass				
Wing top				
Wire gauze with asbestos center				

Laboratory equipment received

Pupil's Signature

b. Cut out a large question mark from brightly colored paper. Spread rubber cement on the back of the paper. When the cement has dried, paste the question mark in the center area of a large pegboard. By means of string hang various pieces of equipment on the pegboard's hooks. Masking tape may also be used to secure apparatus to the board. On a small strip of masking tape placed beside each item put the name of the apparatus. If the display is ready before pupils start the term, most of the names of the apparatus will be familiar by the time laboratory desks are checked.

c. A suggested procedure for setting up an orderly arrangement of chemicals in the laboratory will be found in appendix *A-4*.

1.03. Safety in the Chemistry Laboratory

Every pupil must be made aware of the dangers of accidents in order to insure the safety of himself and every other pupil in the chemistry laboratory. See appendix *A-1* for detailed information dealing with safety.

a. Hazards in the Laboratory. Teachers should discuss and illustrate where possible the following common hazards (see references *1R-6-7*):

- *Fires*—hair or wearing apparel near open flame
- *Burns*—hot water, glass (hot and cold glass look alike), touching hot iron ring on ringstands
- *Cuts*—improper technique of handling glass tubing and thistle tubes, lack of fire polishing
- *Toxic gases*—(H_2S, CCl_4, Cl_2, HCN, Hg)—Improper ventilation
- *Explosions*—caused by unauthorized experimentation or failure to follow directions
- *Poisoning*—often caused indirectly by eating or drinking in the laboratory

b. **School Policy for Reporting Accidents.** Teachers should make perfectly clear to the pupils the policy to be followed in reporting accidents. Each pupil should be well informed as to what he is expected to do should he become involved in an accident or needed to assist in some way as a result of one (see reference *1R-8*).

c. **Written Reports on Accidents.** It is absolutely necessary that each pupil involved in an accident in the laboratory be responsible for reporting it immediately to the instructor. In addition it is a highly desirable educational technique to require each pupil involved in an accident to prepare a written report of the accident. This report should include the following points:

- Concise description of the accident
- Who was involved
- Description of injuries
- Treatment of injuries
- Chemicals and apparatus used
- Basic cause of the accident
- What could have been done to avoid the accident

d. **Using Film on Safety for Summarization.** The film entitled *Safety in the Chemistry Lab* may be used effectively to point up further and summarize the need for safety in the laboratory. This film may be obtained from the Audio-Visual Center, Indiana University, 1804 East Tenth St., Bloomington, Ind.

1.04. Working in the Chemistry Laboratory

a. **Basic Laboratory Techniques.** The differences among pupils both in intellectual capacity and the ability to work with chemical apparatus safely will require that they perform different laboratory exercises. Some pupils will require maximum supervision for the entire year while others may safely proceed with less close supervision after only a few laboratory sessions. Before proceeding to many of the laboratory experiences and activities suggested in this handbook, all pupils should be instructed in, and have experience with, at least the following laboratory techniques. Naturally, it is not expected that all these would be performed in one laboratory session. Special attention is given to these procedures in appendix *A-3*.

- Using the bunsen burner
- Removing liquids from bottles
- Diluting acids and other liquid reagents
- Reading meniscus
- Boiling liquids
- Using thistle tubes
- Filtering liquids
- Using the analytical or platform or triple beam balance
- Putting glass tubing through stoppers
- Removing powdered chemicals from containers
- Using the hood
- Making and using pipettes
- Cutting and bending glass
- Fire polishing
- Heating test tubes, beakers, flasks
- Collecting a gas heavier than air
- Collecting a gas lighter than air

b. Required Laboratory Preparations and Qualitative Identifications. No specific laboratory exercises are required to be done by all pupils. However, as outlined in the chemistry syllabus, some Regents examination questions may be based upon certain laboratory preparations and chemical tests. Pupils should be acquainted by laboratory experience or teacher demonstration with the procedures and results of the following:

LABORATORY PREPARATIONS

- Oxygen
- Hydrogen
- Chlorine, bromine, iodine
- Hydrochloric acid
- Hydrofluoric acid
- Sulfur
- Sulfur dioxide
- Hydrogen Sulfide
- Nitric acid
- Ammonia
- Carbon dioxide

QUALITATIVE IDENTIFICATIONS

- Oxygen
- Hydrogen
- Chlorine, bromine, iodine
- Chloride, bromide and iodide ions
- Sulfite ions
- Sulfate ions
- Sulfide ions
- Nitrate ions
- Ammonium ions
- Carbonate ions
- Metals (flame tests)
- Metals (sulfide tests)

1.05. Benefits of Science

Reports of current scientific developments should be introduced throughout the chemistry course to stimulate interest and, particularly, to emphasize the dynamic nature of science. Individual and committee reports of new developments familiar to pupils are desirable techniques to employ. See appendix *D* for helpful suggestions to follow in writing a report. Some suggestions for topics are:

- The Salk experiments in developing the polio vaccine
- Isotopes used as tracers in biological and medical research

Pupils may also report on chemical discoveries and applications that have produced outstanding changes in man's mode of living. Some examples might include:

- The development of mineral fertilizers by Leibig
- Perkins' discovery of the dye, mauve
- The synthesis of alizarin
- The synthesis of indigo

1.06. Classification of Scientific Information

a. Display specimens of copper, iron, mercury, silver, lead, zinc, aluminum, sulfur, iodine, red phosphorous and carbon. Have pupils classify these elements on various bases such as:

Physical Characteristics	*Chemical Characteristics*
Color	Reaction with water
Apparent heaviness (specific gravity)	Ability to burn
Solubility	

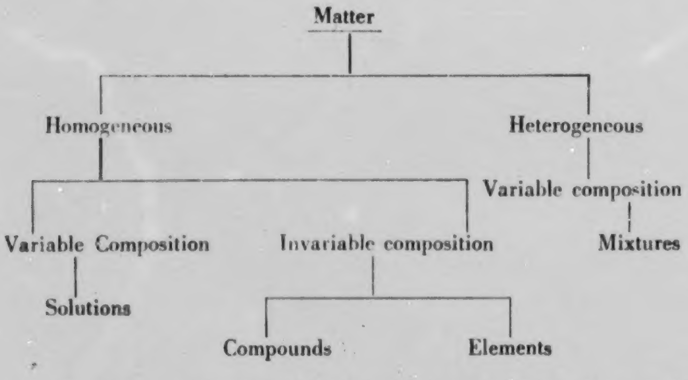
From these various properties, develop systems of classification.

b. Demonstrate the need for the classification of scientific information by displaying a series of compounds such as: sugar, sodium chloride, calcium sulfate, copper sulfate, potassium hydroxide, calcium hydroxide, ammonium chloride, ammonium bicarbonate and sodium carbonate. Illustrate differences in solubility, odor, reaction to litmus and others. Develop a system of classification for these compounds. Determine why a system of classification is desirable.

1.07. Substances

a. A substance is defined as "a homogeneous species of matter with reasonably definite chemical composition." The wording employed should make it obvious that caution should be taken before teaching or accepting oversimplified concepts. When simple definitions are given, they should be undermined later by bringing out exceptions and complications because a simple picture of nature is not a true picture.

The following organization is offered with precautions:



b. Advanced students should be introduced to further concepts such as "system," "phase" and "state" (stable, metastable, unstable).

c. Emphasize that in practice purity is often very difficult to achieve. Some transistor crystals are highly purified; for example, indium antimonide has been brought to a purity of 99.999999 + percent. But even 0.000001 percent of Avogadro's Number is a large amount of impurity. Exhibit the labels of bottles of chemicals that indicate limits of impurity. The development of purer materials is a true frontier of chemistry, in both theoretical and applied respects.

Examples of some of the problems are as follows:

- Supposedly pure sulfur, whose boiling point has been one of the defining temperatures on the international temperature scale, was recently found to contain heavy hydrocarbons. When these are taken out, sulfur melts 0.7° higher than any value reported in the literature.
- Mercury is used as a pressure standard. Pressure is commonly defined in terms of a column of mercury of specified density under specified conditions at a specified height (760 mm.).

Although mercury is easily purified chemically, it has eight or nine isotopes, and isotopic composition varies slightly. Thus, the density does, too, although the variations are only parts per million, and present isotopic abundance measurements are not accurate enough to specify isotopic composition of the mercury used in such measurements.

- There is no krypton available which does not contain krypton-85.
- Aluminum, commonly used to package materials for protection against radiation, contains iron, copper, manganese, zinc and chromium, all of which absorb neutrons.

1.08. The Chemical Elements

a. Exhibit copper in the form of a mixture (a penny or any brass object), a compound (blue copper sulfate) and a pure element (electric wire). Arrange similar displays of other common elements in such forms. Point out to the pupils that they are already familiar with many elements: unalloyed metals, charcoal and oxygen.

b. To increase the pupil's awareness of purity, exhibit in order, cement, glass, quartz, ferrosilicon alloy, commercial silicon and a silicon diode or transistor. Point out the increasing purity of the silicon in this series, but stress the point that *absolute* purity is extremely rare. The best chemical tests for the presence of impurities are relatively crude. Physical tests, such as spectrographic analysis are much better, but they also have their limits. Note that if a gram of iron is one millionth of a percent impure, the atoms in the gram that are not iron number more than 10^{14}. Yet this amount of impurity is not easily detected.

c. Prepare an exhibit of all the elements available in the laboratory. A permanent display of small samples fixed in place on a periodic chart is a superior teaching device.

d. Contrast the Greek concept of the universe as consisting of a few "elements" with the 100-plus chemical "elements" of today. Point out that to the modern physicist there may be only two or three stable "elements": electron, proton and photon. The elements of chemistry are not true ultimates of the universe, yet most of the universe is one of them: hydrogen.

e. Discuss the abundance of the elements in the whole earth and the known crust in terms of weight and in terms of number of atoms (see references *1R-9-10*). Encourage artistic pupils to prepare colored circle graphs to dramatize the inequality of distribution. Make a collection of articles on the project to penetrate the earth's crust to new levels, the "mohole" (see reference *1R-11*). Our present knowledge rests on the monumental work of two scientists connected with the National Bureau of Standards, Clarke and Washington (see reference *1R-12*).

f. Encourage pupils to investigate modern theories concerning the origin of the heavier elements from hydrogen in the stars (see reference *1R-13*). One theory holds that Jupiter is "a stone in a snowball" —a stony core surrounded by a vast mantle of ice and, topping the ice, an 8,000-mile-thick shell of frozen hydrogen. Smaller planets such as Earth, may have had more hydrogen at one time, but being less massive they are less able to hold light elements.

g. Have a committee of pupils interested in premedical studies prepare a chart of the abundance of the elements in the human body. Another group could investigate the composition of sea water and compare it with the composition of blood (see reference *1R-14*).

1.09. Manmade Elements

a. **Below Uranium.** Scientists have produced hundreds of isotopes, stable and unstable, including gold, by addition to and subtraction from existing nuclei. Most of these isotopes represent forms that do not exist naturally, but they may have existed when the earth was more radioactive than now. Four of them, astatine, francium, technetium and promethium have no stable isotopes, but astatine and francium may occur in nature as members of a decay series. Note that the hydrogen isotope, tritium, manmade in sizable quantities, occurs in nature in minute quantities.

b. **Beyond Uranium.** Note that neptunium and plutonium do occur in nature as trace amounts in uranium ores. Curium was discovered before americium, although it comes after it on the table (see references *1R-15-16*). Note that the discovery of element 102 by Swedish chemists has been challenged. Discovery has been claimed by American chemists. The name "nobelium" is not yet official. Most of these elements were identified before they were ever seen; we may never see some of the heavier ones. See references *1R-17-18* on methods of isolating these elements. It is now felt that element 103, "the last of the actinides," will be made. Due to increasing instability it may be the last of the "manmade elements."

c. Some pupils apparently get the impression that manmade elements will soon become household articles. Be sure to point out that with the exception of plutonium which can be used in bombs or reactors, interest in these elements is largely intellectual, and most of them will probably never appear in commercial quantities.

1.10. The Lanthanide Elements

These elements, once lumped together as the "rare earths," are rare no longer and represent a true frontier of modern chemistry. Before World War II these elements and their compounds had a few common uses (see reference *1R-19*). Now they are produced in tonnage quantities and are used in the glass, ceramic, electronic, nuclear and plastic industries. Have the pupils develop an information file on this emerging field. Watch for articles and advertising in *Chemical and Engineering News* (see appendix *F*). Progress in separating these elements from each other has been stepped up by use of ion-exchange resins and chelating agents. Their high price is due, in part, to present slow techniques. For example, it may take four months to pass a band of yttrium salts through an ion exchange column. Some of the lanthanides seem destined for important roles in the utilization of nuclear energy.

Advanced students should be encouraged to analyze the orbitals that give rise to the lanthanide and actinide series (see *Area 2*).

1.11. Compounds

a. The key ideas to be developed here are the changes brought about when:

- Elements combine with one another
- The same elements are combined with bonds of different types (hydrogen chloride and hydrochloric acid)
- The same elements combine in different ratios (H_2O and H_2O_2)
- The same elements in the same ratio are combined in a different sequence (structural isomers)
- The same elements in the same ratio and sequence are combined in a different spatial arrangement (stereoisomers)

Many illustrations of these points can be selected from this handbook. Note also the precautions about defining compounds in "nonstoichiometric compounds."

b. Analysis and synthesis should reappear often in the chemistry course, and many examples will be found in this handbook. Prepare a display of "analytical tools of the chemist" and "products of synthetic chemistry."

1.12. The Law of Definite Composition

A procedure that may be used to illustrate the concept, *definite proportions by weight, follows.*

Iron unites with sulfur in the ratio of 56:32 parts by weight. Place a mixture of 56 gm. of iron filings and 32 gm. of powdered sulfur in a test tube, and heat until incandescence takes place within the tube. Break the tube under cold water and test the FeS with a magnet. Repeat the experiment using an excess of iron. The iron which did not enter into chemical union can now be detected by the magnet.

This exercise lends itself to a discussion of the methods of science and experimental error. In the first step, some sulfur may be volatilized and the results may not be consistent. It is desirable to have each pupil perform this exercise (using one-tenth of the above quantities) and to compile a table of class results that can be used to discuss the experiment statistically.

1.13. Identification of Elements

a. See the sections on analysis for anions, cations and general unknowns in *Area 5*. Use of "unknowns" of various types should be a feature of student laboratory work *throughout* the course rather than lumped into one section at the end. Memorization of specific testing methods, however, is not an objective of this course. Many of these can be summarized on charts for pupil reference instead of being committed to memory. However, maximum laboratory experience in this phase of work is desirable.

b. Books on "commercial analysis," "food analysis" and "physiological chemistry" will provide many very simple tests for pupil laboratory work. Do not overlook possibilities such as testing:

- Soap for free alkali
- Soap for carbonates
- Soap for rosin
- Baking powder for CO_2
- Apples for vitamin C
- Paint for water
- Paint for lead
- Soil for *pH*
- Natural water for *pH*
- Natural water for turbidity
- Various textiles

c. Note that color change is not necessarily a sign of chemical change and colors by themselves are an unreliable means of identification. Color is a physical property and in some cases changes with temperature or stress.

d. Develop an awareness of "interfering substances." This can be accomplished by planting some interfering substances in "unknowns" or by reading to the class a few procedures from an advanced text on analysis to illustrate the precautions taken by the chemist.

1.14. Mixtures

Mixtures should be defined in such a way as to make clear that they include solutions, colloids and systems composed of phases. Point out that the study of mixtures is the culmination of the previous study of pure substances; that it is of the greatest practical importance and that it represents one of the most difficult areas in chemistry. Understanding of mixtures and their separation should not be taken for granted. A worthwhile pupil exercise or a teacher demonstration is imperative.

a. Prepare a mixture of washed sand and salt. Vary the proportions by adding more of one or the other component. Taste the mixture to show that the characteristic property of the salt has not been altered. Add water to the mixture, stir, and filter. The residue is the original sand. Evaporate the salt solution to dryness over a bunsen burner to obtain the original salt. This activity shows that mixtures may be prepared in any proportions and that they can be separated into their component parts by using physical means.

b. A mixture of sulfur and iron filings can be separated by adding carbon disulfide followed by filtration and evaporation. This should be done by allowing the mixture to stand in the hood.

c. Display a number of common mixtures such as: soil, concrete, milk, paint, air and kaolinite in water. Discuss how they may be separated by physical means.

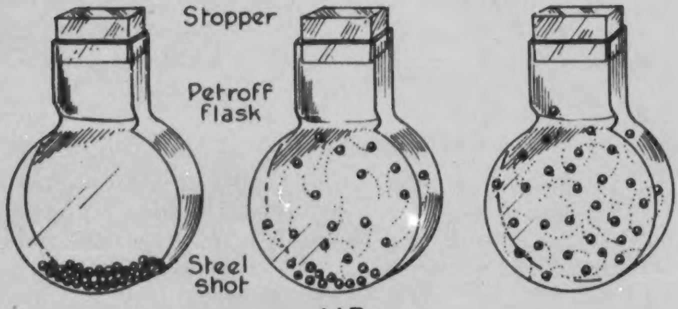
1.15. Kinetic Molecular Theory

a. Exhibit clear glass bottles of iodine crystals and liquid bromine to show the vapor phase present in each case. Place stoppered bottles containing water concentrated with ammonia and concentrated hydrochloric acid alongside and discuss the presence of vapor above these liquids too. Remove the stoppers from the ammonia and acid to confirm the presence of invisible vapors by the formation of ammonium chloride smoke.

b. Illustrate sublimation by warming some iodine crystals in a large dry flask. Relate to sublimation of moth flakes and snow. *Use hood.*

c. Illustrate molecular motion on the overhead projector and relate to temperature and state (see diagram 1.15*c*).

d. Some people term ionized gases a "fourth state" of matter called *plasma*. The term plasma is not yet strictly defined. Ask for a report to the class on recent developments.



1.15c

e. Saturate about 50 ml. of water with potassium nitrate at a temperature of 60°C. Pour a thin layer into a petri dish on the overhead projector, and allow to cool and crystallize during the period. Discuss the effect of loss of heat (kinetic energy) on the formation of the solid state.

f. Discuss recent developments in solid state chemistry, a new frontier (see reference *1R-20* and appendix *D*).

1.16. Chemical Symbols

a. Symbols of the Common Elements. Pupils should master early in the course a basic list of the symbols of the most common elements. These include:

Aluminum—*Al*
Antimony—*Sb*
Barium—*Ba*
Bromine—*Br*
Calcium—*Ca*
Carbon—*C*
Chlorine—*Cl*
Chromium—*Cr*
Cobalt—*Co*
Copper—*Cu*
Fluorine—*F*
Gold—*Au*
Hydrogen—*H*
Iodine—*I*
Iron—*Fe*
Lead—*Pb*

Magnesium—*Mg*
Manganese—*Mn*
Mercury—*Hg*
Nickel—*Ni*
Nitrogen—*N*
Oxygen—*O*
Phosphorus—*P*
Platinum—*Pt*
Potassium—*K*
Silicon—*Si*
Silver—*Ag*
Sodium—*Na*
Strontium—*Sr*
Sulfur—*S*
Tin—*Sn*
Zinc—*Zn*

b. **Quantitative.** Stress that the symbol:

- Identifies the element
- Represents one atom of the element (if the context implies this usage)
- May represent one "standard quantity," or mole, of the element (if such is implied in the context)

c. **Isotopic Symbols.** Point out the growth of a new symbolism in our day although usage is not yet uniform. Radioactive hydrogen, tritium, for example, may have the symbol, T, H^3, ${}_1H^3$ or ${}^3H$. Inclusion of atomic numbers with symbols is redundant to experienced chemists, but is useful to pupils in any introductory course.

1.17. Formulas

a. **What the Formula Represents.** The formula is a shorthand understood by chemists of all nations. It is a qualitative expression for a compound, as the symbol is for the element. It is even more quantitative than a symbol. The formula:

- Tells how many atoms of each element are present
- May represent a complete molecule (for example, CH_4) or a ratio of ions (for example, NaCl)
- May stand for one molecule, one molecular weight, one formula weight, or one mole quantity
- May tell little or nothing about structure (for example, Na_2SO_4) or may reveal something about how the atoms are arranged (for example, $CH_3CH_2CH_3$)

Note: Two systems of nomenclature are used throughout the handbook since no one system has been adopted universally. For example, $CuSO_4$ is referred to as either (1) cupric sulfate or (2) copper (II) sulfate.

b. **Writing Chemical Formulas.** From red and blue cardboard cut three red and three blue 4-inch circles. Label one red circle *Na*, the second *Mg* and the third *Al*. In a similar manner label the blue symbols *O*, *Cl* and *S*. From felt make seven blue and three red 1-inch circles, three blue plus (+) symbols and three red minus (—) symbols (see appendix *B-3*).

Refer the pupils to the Periodic Table, and point out the electronic structure. Mention that the formation of a compound depends upon the rearrangement of the electrons in the reacting atoms so that each atom can have completed shells. Call all the atom, except the valence electrons, the core. Point out that the core of an atom contains completed shells in addition to the nucleus. The electrons in the incompleted shells are called ***valence electrons.***

Place the circle representing the sodium core and a red circle (valence electron) on the felt board. Then put a chlorine core and seven blue electron circles on the felt. Remind the pupils that the cardboard circles contain only completed shells and that ring completeness must be obtained for all atoms undergoing chemical action. Ask the pupils to suggest a way to obtain completed ring structure for the sodium and chlorine atoms represented on the felt board. Then transfer the red circle over to the area where the blue electron circles are. Using information found on the periodic table, have the pupils figure out the electric charge that has been placed upon each atom as a result of the electron transfer. Place the charge by each ion on the felt board. Relate the shifting of electrons to valence and oxidation number.

Note: A distinction between the terms *valence* and *oxidation number* may be found in recent high school and college chemistry texts. On the chalkboard using oxidation numbers write the formula for sodium chloride. Compare the information given by the formula and by the materials on the felt board.

Using the above procedure, develop the formulas for sodium sulfide, magnesium oxide, magnesium chloride, aluminum chloride, aluminum sulfide and aluminum oxide. (At this point the teacher may choose to represent the sulfur molecule as composed of one atom instead of eight.)

When using the felt board it is not advisable to select atoms having more than one oxidation number since it is difficult to illustrate the reason that some elements have more than one oxidation number (*oxidation state*) in this situation. Orbital and subshell diagrams prove to be more effective in explaining why the reaction occurs.

c. **Mathematical Applications.** When the writing of formulas and the concept of molecular or formula weight are understood, it is suggested that appropriate mathematical applications be introduced. Pupils should continue to make these applications whenever possible throughout the course. (See appendix *E*.)

(1) *Calculate the formula weight of* $(NH_4)_2SO_4$.

Weight of 2 atoms of nitrogen = 2 x 14.01 = 28.02
Weight of 8 atoms of hydrogen = 8 x 1.008 = 8.064
Weight of 1 atom of sulfur = 1 x 32.07 = 32.07
Weight of 4 atoms of oxygen = 4 x 16.00 = 64.00

Formula weight = 132.154 = 132.15

(2) *Calculate the percentage of oxygen by weight in $KClO_3$.*

Weight of K = 1 x 39.10 = 39.10
Weight of Cl = 1 x 35.46 = 35.46
Weight of O = 3 x 16.00 = 48.00

122.56 = 122.56

$$\text{Percentage of oxygen} = \frac{48.00}{122.6} = 39.15\%$$

(3) *Calculate the weight of oxygen in 100.0 pounds of $KClO_3$.*

Percentage of oxygen by weight = 39.15% *(see previous problem)*

Amount of oxygen = 100.0 lb. x 0.3915 = 39.15 lb.

(4) *The composition by weight of a compound is 85.7 percent carbon and 14.3 percent hydrogen. The molecular weight is 56. Determine the formula:*

$$\text{carbon} = \frac{85.7}{12.0} = 7.14$$

$$\text{hydrogen} = \frac{14.3}{1.00} = 14.3$$

$$\frac{\text{carbon}}{\text{hydrogen}} = \frac{7.14}{14.3} = .499 = \tfrac{1}{2} \text{ (approximately)}$$

In the formula the ratio of carbon atoms to hydrogen atoms is 1:2. The formula may be CH_2, C_2H_4, C_3H_6, C_4H_8, C_5H_{10} and so on. Of these, C_4H_8 has a molecular weight of 56.

An alternate approach might be:

$$\text{carbon} = \frac{85.7}{12.0} = 7.14, \quad \frac{7.14}{7.14} = 1.00$$

$$\text{hydrogen} = \frac{14.3}{1.00} = 14.3, \quad \frac{14.3}{7.14} = 2.00$$

Note: Ratio of atoms must be whole numbers.

1.18. Working with Chemical Equations

a. Writing and Balancing Chemical Equations. The need for balancing equations can be understood easily by pupils when a felt board is used to illustrate the process (see appendix B-3).

Prepare the materials needed for using the felt board. Cut out six 3 x 5-inch felt rectangles; three blue, two red and one brown. Make six gray and six yellow circles about 1 inch in diameter. Print a set of cards, one card for each formula or coefficient that is to be used in sample equations, two cards with arrows and two cards with plus symbols.

Illustrate the equation for reacting aluminum and sulfur. (For simplicity the teacher may choose to represent the sulfur molecule as composed of one atom instead of eight.) Place on the felt board the red rectangle. Show it stands for an aluminum molecule by placing the formula card below it. Then arrange a gray circle on the red felt to show that the aluminum must have one atom per molecule. Point out that the formula also shows one atom per molecule. In a similar manner arrange a blue rectangle with a yellow circle to illustrate the sulfur molecule, and label it with the formula card. Put a plus symbol and arrow in the proper position to indicate a reaction is occurring between the felt molecules. Next put the brown rectangle on the felt board, and ask the pupils to tell the name and formula of the substances formed. Identify the brown figure with a formula card. Note that three yellow and two gray circles must be added to the brown rectangle before it can represent aluminum sulfide. Require the pupils to suggest the only way of obtaining these circles. Then place the extra rectangular molecules before the arrow, and transfer the circles to the brown felt. Note that all the atoms required to produce aluminum sulfide have been supplied by the combining molecules. Count the number of red aluminum rectangles, and place a corresponding coefficient card in front of the aluminum formula card. Repeat the process for the other two materials, and complete the card equation by adding the plus sign and arrow. Draw the pupils' attention again to the fact that the reaction has used all the atoms that originally were in the reacting molecules and that a definite amount of molecules was needed to supply the required number of atoms. Show how coefficients can be used to describe the number of molecules and to figure the number of atoms involved in the reaction. On the chalkboard write the equation in the usual manner and balance it.

Among other equations that can be illustrated, those for oxygen and aluminum, oxygen and magnesium or chlorine and sodium are effective examples for felt board presentation of equation writing.

If double or single replacement reactions are used for examples, extra sets of different colored rectangle(s) and circles will be needed.

b. Mathematical Applications. When the balanced equation is understood, the typical *weight—weight* problem should be introduced. Appropriate problems should be solved throughout the entire course.

What weight of hydrogen is produced when 150.0 grams of zinc react completely with an excess of hydrochloric acid?

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

Substitution in the balanced equation results in the following relationships:

$$\frac{\text{weight of Zn}}{\text{equation weight of Zn}} = \frac{\text{weight of } H_2}{\text{equation weight of } H_2}$$

$$\frac{150.0 \text{ gm.}}{65.38} = \frac{x}{2.016}$$

$$x = \frac{2.016 \times 150.0 \text{ gm.}}{65.38} = 4.624 \text{ gm.}$$

c. **Further Mathematical Applications.** When the concept of the mole and its equivalence to 22.4 liters of a gas are understood, further applications are possible.

(1) *What volume of hydrogen is produced when 150.0 grams of zinc react completely with an excess of hydrochloric acid?*

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2$$

$$\frac{\text{weight of Zn}}{\text{gram molecular weight of Zn}} = \frac{\text{volume of } H_2}{\text{gram molecular volume of } H_2}$$

$$\frac{150.0 \text{ gm.}}{65.32 \text{ gm.}} = \frac{x}{22.4 \text{ l.}}$$

$$x = \frac{22.4 \text{ l.} \times 150.0 \text{ gm.}}{65.32 \text{ gm.}} = 51.4 \text{ l.}$$

Note that this method is an extension of the problem in *b* above in which the volume of the 4.624 gm. of hydrogen is computed.

$$\frac{2.016 \text{ gm.}}{22.4 \text{ l.}} = \frac{4.624 \text{ gm.}}{x}$$

$x = 51.4$ l.

(2) *What volume of hydrogen will combine with 40 liters of oxygen to form water vapor?*

$$2H_2 + O_2 \rightarrow 2H_2O$$

The equation states that 4.032 gm. (44.8 l. or 2 moles) of hydrogen react with 32.00 gm. (22.4 l. or 1 mole) of oxygen to produce 36.03 gm. (44.8 l. or 2 moles) of water vapor.

One of three possible relationships is:

$$\frac{\text{volume of } H_2}{\text{moles of } H_2} = \frac{\text{volume of } O_2}{\text{moles of } O_2} = \frac{x}{2 \text{ moles}} = \frac{40 \text{ l.}}{1 \text{ mole}}$$

$x = 80$ l.

(3) *Calculate the approximate density of oxygen gas.*

22.4 l. of oxygen gas (O_2) weigh 32.00 gm.

$$\text{density} = \frac{\text{weight}}{\text{volume}} = \frac{32.00 \text{ gm.}}{22.4 \text{ l.}} = 1.43 \text{ gm./l.}$$

(4) *What is the weight of one mole of a gas if 400 ml. of the gas weigh 0.607 gm. at S. T. P.?*

$$\frac{\text{weight}}{\text{volume}} = \frac{\text{gram molecular weight}}{\text{gram molecular volume}}$$

400 ml. = 0.400 l.

$$\frac{.607 \text{ gm.}}{.400 \text{ l.}} = \frac{x}{22.4 \text{ l.}}$$

$$x = 34.0 \text{ gm.}$$

1.19. Physical Changes

Physical changes are those in which the identifying properties of substances remain unchanged. There may be a change in form, state or energy level. Demonstrate that no permanent change occurs in the properties of the substance during physical changes.

a. Place 100 ml. of water in a 250-ml. beaker. Cover with a watchglass and heat. Call attention to the condensation of steam back to water.

b. Dissolve sugar in a beaker of water. Recrystallize the sugar by evaporating water from the solution. This may be speeded up by placing some of the solution on a watchglass and heating it gently.

c. Break a wood splint. Ask pupils to identify the material in each part.

d. Magnetize a nail by stroking it with a permanent magnet. Demonstrate its new magnetic properties with iron filings. Heat the nail gently to demagnetize.

e. Tear a piece of paper into sections, or stretch a rubber band to illustrate a change of shape but not of properties.

f. Sublime some naphthalene (mothballs) or some paradichlorobenzene.

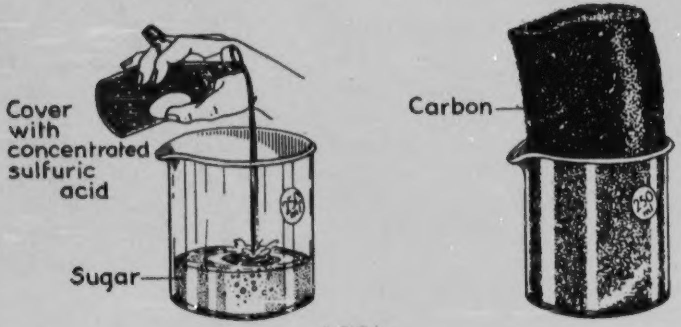
g. Sublime some iodine crystals by heating them gently in an evaporating dish covered with a watchglass or inverted funnel.

1.20. Chemical Changes

Chemical changes are those in which new substances with new characteristics are formed. These changes may result from (1) the combination of atoms, (2) breaking down of complex substances into simpler compounds and (3) compounds that may react with other compounds or elements to form different compounds.

a. TEACHER DEMONSTRATION ONLY: On an asbestos pad, heap a 20-gm. pile of ammonium dichromate. Ignite it with a bunsen burner. This makes a small "volcano" with the formation of the green chromium oxide. If the room is darkened, this reaction makes an effective and spectacular demonstration illustrating chemical change.

b. TEACHER DEMONSTRATION ONLY: Place ½ inch of sugar in a beaker and cover it with concentrated sulfuric acid (see diagram 1.20*b*). Compare the properties of the sugar before the reaction (white, soluble) with the properties of the residue (black, insoluble). *CAUTION: Must be performed under the hood.*


Cover with concentrated sulfuric acid
Sugar
Carbon
250 ml

1.20b

c. TEACHER DEMONSTRATION ONLY: Mix thoroughly 2 gm. of flowers of sulfur and 1 gm. of zinc dust. Heap the mixture onto an asbestos mat and place a 2-inch length of magnesium ribbon upright in it. Ignite the magnesium ribbon by means of a burner. The burning fuse provides a second or two to depart before the mixture erupts in a spectacular combustion. *CAUTION: Perform under the hood.*

d. Place a clean strip of iron or an iron nail into a saturated solution of copper sulfate. The iron is plated with copper, and the color of the solution changes.

e. An excellent example of a chemical change involves examining a few crystals of common salt (sodium chloride) and noting the physical characteristics. Add a few drops of silver nitrate solution to a salt solution, and note the white precipitate which turns dark upon exposure to direct sunlight.

1.21. Difference between Chemical and Physical Change

Cut a piece of clean magnesium ribbon, 3 to 4 inches in length. Demonstrate its physical properties to the class: color, flexibility and insolubility.

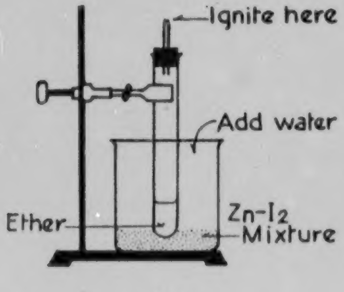
Using chemical tongs, hold the magnesium ribbon in a bunsen flame. Call attention to the intense light emitted, heat evolved and the properties of the powdered residue. *CAUTION: Do not look at the intense light except for a very brief moment.*

1.22. Energy Releases During Chemical Change

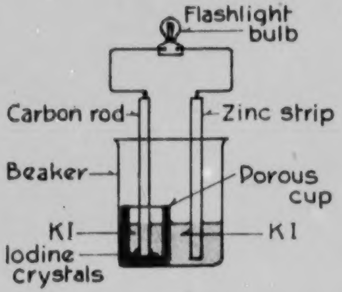
a. **Heat Energy Release.** *TEACHER DEMONSTRATION ONLY:* The purpose of this exercise is to show that the union of zinc and iodine produces heat energy. *CAUTION: Perform under hood.*

Prepare a zinc-iodine mixture in a beaker by grinding together 14 gm. of iodine crystals with 2 gm. of zinc grains or zinc dust. Use a vertical tube containing ether. A jet is inserted at the top of this tube (see diagram 1.22*a*). Add *exactly* 3 ml. of water to the powdered mixture of iodine and zinc; this amount of water is critical. The heat generated will vaporize the ether. Ignite the ether at the top of the tube.

b. **Electrical Energy Release.** Prepare a voltaic cell according to diagram 1.22*b*. The porous cup contains 80 ml. of a 15 percent solution of potassium iodide. The cup should be soaked in a potassium iodide solution about 30 minutes before use. The cup is placed in a 400-ml. beaker which contains 140 ml. of a 15 percent solution of potassium iodide. About 14 crystals of iodine are added to the porous cup with stirring.



1.22a



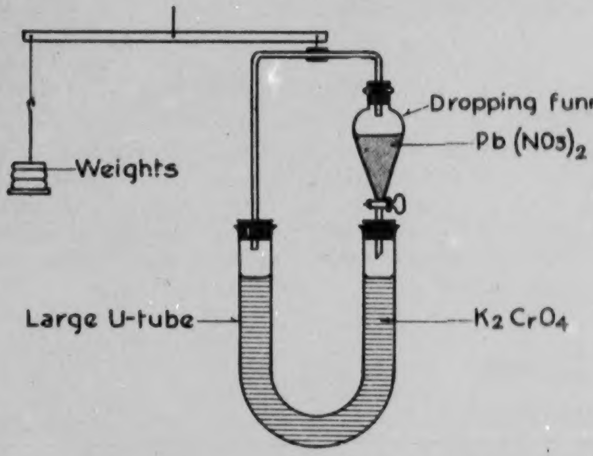
1.22b

The electrode in the cup consists of a carbon rod; it should be stirred into the excess iodine crystals on the bottom of the cup to insure good contact. The other electrode consists of a strip of zinc. Battery clips from the electrodes lead to an external circuit which consists of an incandescent light bulb. A 1.1, 2.2 or 3.8-volt bulb required for a flashlight will prove satisfactory. When connected, the bulb lights immediately, showing that the cell is producing electricity.

1.23. Conservation of Mass in a Chemical Change

The apparatus in diagram 1.23 effectively shows that no loss in mass occurs during a chemical reaction and at the same time eliminates a remassing operation. (See also activity 6.14*a*.)

A large U-tube and a dropping funnel are its essential components. The tube and the funnel hold solutions that will react with each other when mixed, such as lead nitrate and potassium chromate. This apparatus is suspended from one arm of a counterpoised balance, and the stopcock is then opened.



1.23

1.24. Endothermic Reactions

A reaction in which heat is absorbed is an *endothermic* reaction.

a. Use the decomposition of mercuric oxide (Priestley's classical experiment) to illustrate this type of reaction. Heat with a bunsen burner ½ teaspoon of mercuric oxide in a pyrex test tube. Test the gas evolved with a glowing splint. Call attention to the mirror of mercury (globules of Hg) formed on side of test tube.

b. On a wet block of hard wood (2 inches x 2 inches x ⅛ inch), place a 250-ml. beaker containing approximately 50 gm. of ammonium nitrate. Add 50 ml. of water while stirring vigorously. The beaker will freeze to the block of wood.

c. Place 50 gm. of crystalline sodium sulfate in a 250-ml. beaker. Add 25 ml. of concentrated hydrochloric acid, and record the temperature change. The temperature will drop from about 20°C to about –5°C.

1.25. Exothermic Reactions

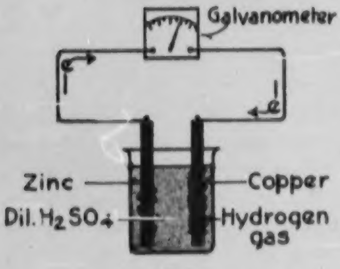
A reaction in which heat is liberated is an *exothermic* reaction.

a. Fill a collecting bottle three-fourths full of hydrogen gas. Permit air to mix with the hydrogen for several seconds and then ignite the mixture with a burning splint. The "pop" indicates that a chemical reaction has taken place with the release of energy. Ordinary illuminating gas direct from the gas jet may be substituted for the hydrogen gas with the same results. *CAUTION:* Wrap bottle in towel.

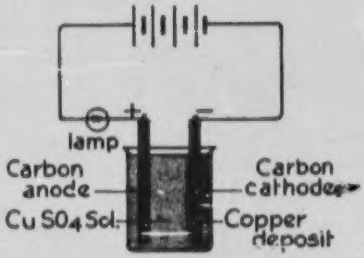
b. Burn a wood splint, burn a cube of sugar, and eat a cube of sugar in front of the class. In all three cases a chemical change has taken or will take place in which energy is released. Discuss these changes.

1.26. Changing Chemical Energy to Electrical Energy

Place a strip of copper and a rod of pure zinc in a beaker containing dilute sulfuric acid (acid:water = 1:6). Connect the two metals to a galvanometer as shown in diagram 1.26. The deflection of the galvanometer needle indicates that there is a flow of electrons from one metal to the other. *Note:* If impure zinc is used as an electrode, bubbles appear, indicating a reaction between the zinc and the acid. When the circuit is completed through the galvanometer, bubbles will appear on each electrode.



1.26



1.27

1.27. Absorption of Electrical Energy

The electroplating of a metal illustrates the absorption of electrical energy. To plate with copper, use a saturated solution of copper sulfate. A three-molar solution of silver nitrate is satisfactory to illustrate silver plating. Any source of direct current from 6 to 40 volts is adequate. The cathode may be chemically cleaned by dipping into an acidified bichromate solution and then rinsing it. A lamp in series with the apparatus will show when the circuit is closed (see diagram 1.27). Four 1.5-volt dry cells and a miniature lamp all in series produce excellent results. Reverse the direction of current and observe result.

1.28. Absorption of Mechanical Energy

a. Grind some crystals of silver chloride vigorously in a mortar. Silver metal and gaseous chlorine are formed. Note the odor.

b. Grind together some solid mercuric nitrate and solid potassium iodide. The change in color indicates a reaction.

1.29. Liberation of Light Energy

a. Demonstrate any example of rapid oxidation such as the burning of magnesium ribbon or burning of wood. (Caution pupils not to look directly at the burning magnesium.)

b. Use any of the examples given in activity 1.22 in which chemical energy is converted into both heat and light energies.

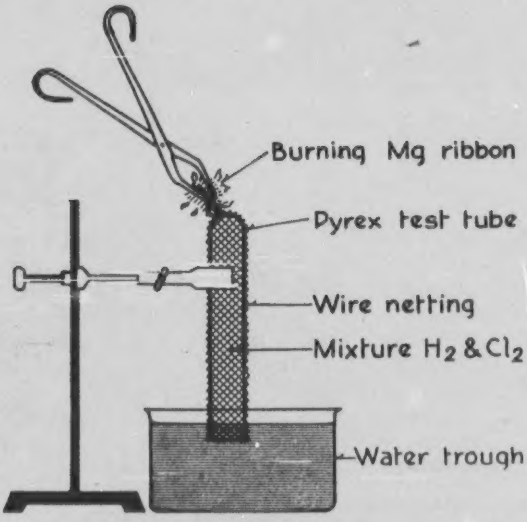
c. Dry some corn starch over a register or gentle heat. Place about ½ teaspoon into a rolled sheet of paper and blow dust directly into a bunsen flame. Lycopodium powder may be similarly employed.

1.30. Chemiluminescence

Mix equal volumes of the following in a 1-liter flask: 3 percent hydrogen peroxide, 0.01-molar solution of pyrogallol and 0.01-molar solution of potassium permanganate. In a darkened room, the mixture will glow for a short time.

1.31. Absorption of Light

a. TEACHER DEMONSTRATION ONLY: Collect a pyrex test tube half full of chlorine and half full of hydrogen using the usual water displacement procedure. The two gases do not combine unless exposed to a source of intense light. Next bring a burning piece of magnesium ribbon near the test tube. The hydrogen and chlorine will combine *VIOLENTLY* to form hydrogen chloride. The HCl will dissolve readily and the test tube fills with water (see diagram 1.31*a*).



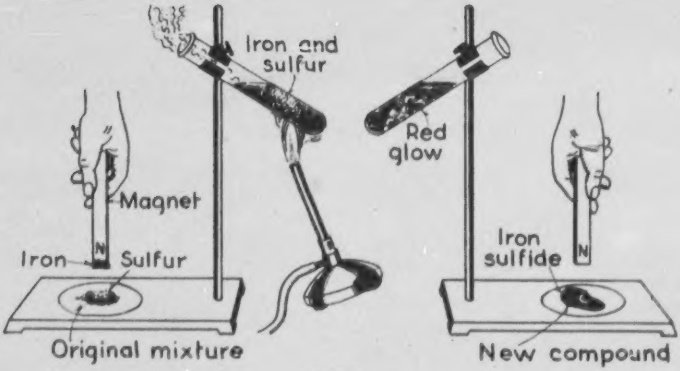
1.31a

CAUTION: Cover test tube with a protective mantle of fine wire netting; use glove when bringing burning magnesium near test tube.

b. Obtain a sheet of "studio proof" photographic paper. This paper may be handled in ordinary light. Cover ½ sheet with an opaque material or a film negative, and expose to either direct sunlight for three to four minutes or to a 4-inch piece of burning magnesium ribbon. Note darkening effect produced by the absorption of light. The paper will gradually darken on further and continued exposure to light.

1.32. Chemical Changes May Alter Properties

Mix 7 gm. of iron powder or iron filings and 5 gm. of powdered sulfur. Test the mixture with a magnet and point out that the iron and sulfur may be separated in the mixture. Pour the mixture into a pyrex test tube and support the test tube in a clamp on a ringstand. Heat the mixture gently at first and then strongly. Keep the flame in motion so as to heat the tube uniformly. When the contents of the tube begin to glow, remove the heat and call attention to the evidence of a chemical change. When the tube is cool, wrap it in a piece of cloth and break it with a hammer. Test the mass with a magnet to show that a new nonmagnetic substance, iron sulfide, has been formed (see diagram 1.32).

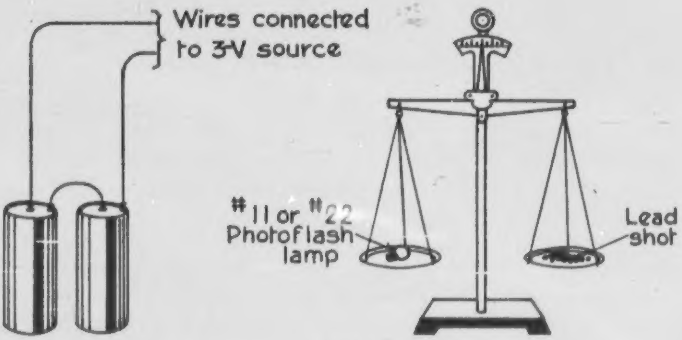

Iron and sulfur
Red glow
Magnet
Iron
Sulfur
Iron sulfide
Original mixture
New compound

1.32

1.33. Conservation of Matter

a. Counterbalance a suspended photoflash bulb on a balance. Ignite the bulb with wires connected to a 3-volt source (two dry cells in series) without removing the bulb from the balance. Call attention to the evolution of heat and light with no evident change in weight (see diagram 1.33*a*). *Note:* The larger size photoflash bulb, *No. 11* or *No. 22*, is suggested.

CAUTION: Check bulb for cracks in the glass; do not use a defective photobulb since it may explode.

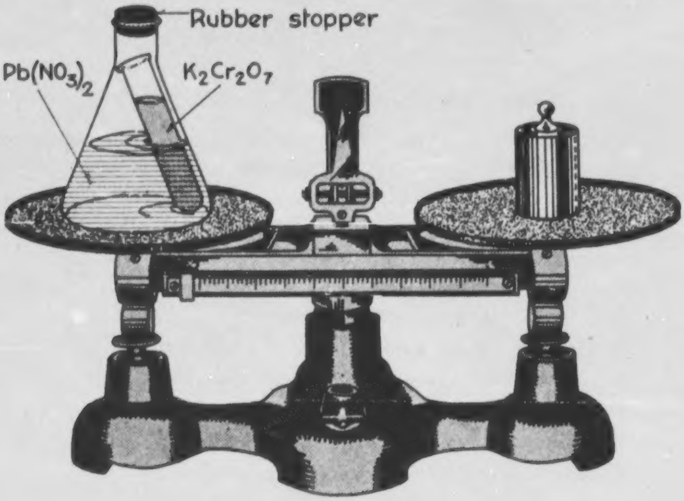

Wires connected to 3-V source
#11 or #22 Photoflash lamp
Lead shot

1.33a

b. Refer to the historical experiments of Lavoisier in which he (1) oxidized a weighed amount of mercury and then obtained the same weight of mercury by the decomposition of the oxide and (2) oxidized tin in a closed system and found no change in weight.

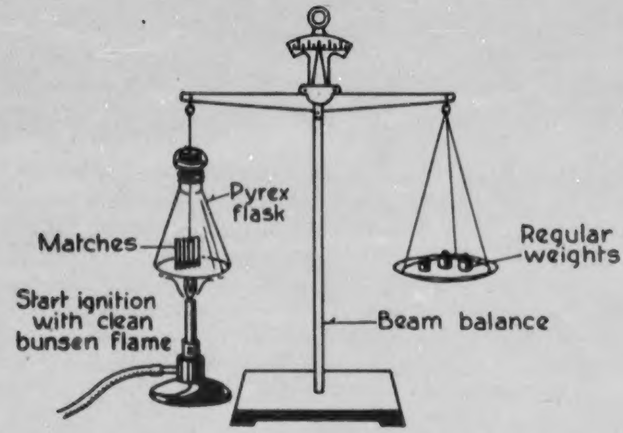
CAUTION: Mercury vapor is poisonous.

c. Place some lead nitrate solution in an Erlenmeyer flask. Insert into this flask a small test tube containing potassium dichromate solution. Stopper the flask, and counterpoise it on a beam balance. Now tip the flask upside down so that the two liquids mix. A yellow precipitate results indicating a chemical change. Replace the flask and the contents on the balance to show that no change in weight has occurred (see diagram 1.33*c*). *Note:* Solutions of barium chloride and sodium sulfate may be substituted for the reactants. A white precipitate will result.



1.33c

d. Ignite a bundle of matches contained in a counterpoised sealed flask by heating the outside with a clean bunsen flame. The mass of the substances involved remains the same before and after the reaction (see diagram 1.33*d*). The tips of the matches should touch the bottom of the flask.



1.33d

1.34. Using Raw Materials

Have pupils prepare charts or flow sheets indicating relationships between end products and the raw materials used in their manufacture. The following is an example:

- Production of nylon (coal, air, water) or "orlon" (coal, air, water, petroleum, natural gas)
- Products produced from crude oil (see chart below)
- Products obtained from soft coal
- Chemicals from rock salt (see chart below)
- Products from limestone (include products made from acetylene)
- The story of cellulose (see diagram 1.34)
- Sulfur, the basic raw material of industry

A further illustration is shown in the chart below.

Rock Salt Products

Sodium		Chlorine
Sodium peroxide Bleaching agents	Synthetic detergents	Hypochlorites
	Tetraethyl-lead	Chlorates
Sodium perborate Pharmaceuticals Dye fixation	Dyes	Water treatment
	Special alloys	Hydrogen chloride

Zinc peroxide
  Bactericide
  Cosmetics

Calcium peroxide
  Commercial baking

Magnesium peroxide
  Pharmaceuticals

Heat transfer

Sodium sulfocyanide

Metal cyanides

Sodium cyanide

Sodium carbonate

Sodium bicarbonate

Sodium hydroxide

Chloroform

Freon refrigerants

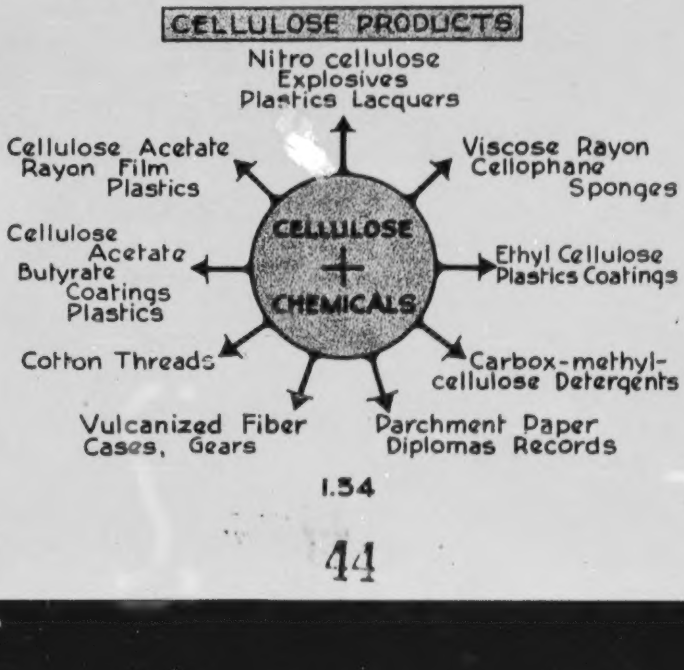
Carbon tetrachloride

Chloroprene

Vinyl chloride

Crude Oil Products

Primary Products	**Polymerization**	**Alkylation**	**Hydrogenation**
Fuel Gas	**Increased gasoline yields**	**Alcohols**	**Aviation gasolines**
Gasoline	**Synthetic gasolines**	**Butadiene**	
Kerosene		**Ethylene**	
Lubricating Oils		**Increased gasoline yields**	
Vaseline			
Paraffin			
Tar			
Petroleum coke			


CELLULOSE PRODUCTS
Nitro cellulose Explosives Plastics Lacquers
Viscose Rayon Cellophane Sponges
Ethyl Cellulose Plastics Coatings
Carbox-methyl-cellulose Detergents
Parchment Paper Diplomas Records
Vulcanized Fiber Cases, Gears
Cotton Threads
Cellulose Acetate Butyrate Coatings Plastics
Cellulose Acetate Rayon Film Plastics
CELLULOSE + CHEMICALS

1.54

1.35. Chemical Industries

Have pupils make a list of industries in the area which are large users of chemicals. Provide for plant visitations. A profitable visit to a local chemical industry could prove a valuable experience (see appendix *C*). Invite representatives of industry to speak to your chemistry classes. Modify the following chart to emphasize the local use of chemicals:

INDUSTRY	CHEMICALS USED	PURPOSE	PRODUCTS PRODUCED

1.36. Chemistry and Conservation of Waste Products

Modern industrial technology makes use of many substances formerly considered as waste products and/or have devised new uses for materials in short supply. Illustrate with examples familiar to the pupils:

- Where SO_2 previously devastated the countryside, it is now converted into the useful sulfuric acid at copper, zinc and lead smelters.
- As a byproduct of the Solvay process, calcium chloride was dumped into Onondaga Lake. It is now used to melt snow and ice on city streets, keep dust down and to serve as a dehumidifier.
- The recovery of silver and gold from the sludge produced in the electrolysis of copper is a profitable source of revenue.
- The shortage of lead is leading to the use of lead-plated metals in storage batteries.
- The slag from the blast furnace is used for roadbuilding materials.
- Technetium, the synthetic element found in the products of uranium fission, is used to inhibit the oxidation of iron.
- Calcium metal and calcium alloys are used as deoxidation substances in the preparation of high-quality steels.
- Solvents are recovered in the dry cleaning process.
- Zinc instead of nickel is used in coin nickel.
- Chlorine is used to recover tin from scrap metal.
- Experimentation is being done with the digestibility of sawdust to produce cattlefeed.

- Cellulose sponges are used to replace the natural product.
- The Fischer-Tropsch catalytic process provides synthetic petroleum. Gasoline yield from oil is increased by cracking, hydrogenation and polymerization.
- Methanol, previously made from wood, is now produced synthetically.

Area 1 References

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1R-2. The place of scientific method in the first course in chemistry. Journal of Chemical Education, v. 28, No. 6: 300. June 1951

1R-3. Teaching the scientific method in college general chemistry. Journal of Chemical Education, v. 34, No. 5: 238-239. May 1957

1R-4. Some demonstrations with the overhead projector. Journal of Chemical Education, v. 35, No. 1: 36. Jan 1958

1R-5. The overhead projection and chemical demonstrations. Journal of Chemical Education, v. 28, No. 11: 579. Nov. 1951

1R-6. Prevention of accidents when handling chemicals. Journal of Chemical Education, v. 27, No. 12: 670-673. Dec. 1950

1R-7. A laboratory safety program. Journal of Chemical Education, v. 29, No. 11: 553. Nov. 1952

1R-8. Safety in chemistry laboratories. Journal of Chemical Education, v. 31, No. 2: 95-96. Feb. 1954

1R-9. The elementary composition of the earth. Journal of Chemical Education, v. 33, No. 2: 67. Feb. 1956

1R-10. The abundance and distribution of elements in the earth's crust. Journal of Chemical Education, v. 31, No. 9: 446-455. Sept. 1954

1R-11. The mohole. Scientific American, v. 200, No. 4: 41. Apr. 1959

1R-12. The great analysis. Journal of Chemical Education, v. 30, No. 11: 566. Nov. 1953

1R-13. The abundance of the elements. Scientific American, v. 183, No. 4: 14-17. Oct. 1950

1R-14. The gold content of sea water. Journal of Chemical Education, v. 30, No. 11: 576-579. Nov. 1953

1R-15. Symposium: the new elements. (7 articles) Journal of Chemical Education, v. 36, No. 1: 2-45. Jan. 1959

1R-16. The synthetic elements. Scientific American, v. 182, No. 4: 38-47. Apr. 1950

1R-17. The first isolations of the transuranic elements. Journal of Chemical Education, v. 36, No. 7: 340-343. July 1959

1R-18. Ultramicrochemistry. Scientific American, v. 190, No. 2: 76-82. Feb. 1954

1R-19. The lanthanide contraction as a teaching aid. Journal of Chemical Education, v. 28, No. 6: 312-317. June 1951

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NOTES

AREA 2

The Atomic Structure of Matter

2.01. Introduction to Atomic Structure

Daily, more and more facts and theories concerning the structure of the atom are being reported in scientific literature and in the press. It has become necessary for most teachers of an elementary chemistry course to present the historical details (prior to about 1920) in a condensed form and stress only the highlights of the discoveries. Details of experiments, theories and biographical data, regardless of their interest and importance, must of necessity be reserved for those pupils who can best profit from such study. The chemistry teacher must also educate himself continuously concerning modern atomic theory and interpret to the pupils the major result of changes in the theory. A detailed, mathematical study of the many recent advances must, for practical reasons, be reserved for advanced chemistry courses (see bibliography).

This area differs from others in this handbook mainly in that it attempts to provide material which has been digested from a variety of sources and to give relatively simple answers to questions commonly asked. Various methods of presentation and associated visual devices are suggested from which the teacher may select material suitable to the abilities and future needs of the pupil. Develop an introductory discussion for the class through the use of an outline.

2.02. Existence of Atoms and Molecules

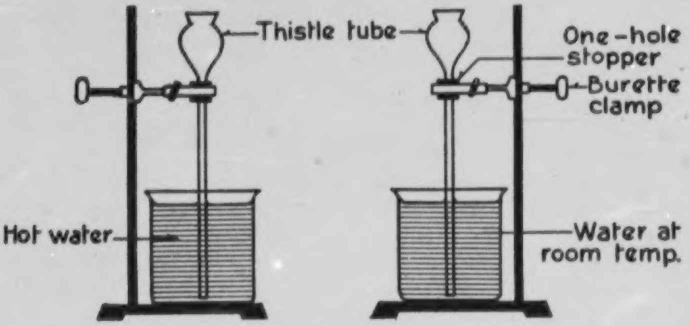
Numerous experiments in the last two centuries have left little, if any, doubt that atoms really exist and that they are small, approximately of the same size, and are in motion. A variety of demonstrations can provide evidence of the kinetic-molecular theory which in turn will increase the understanding of atoms.

a. Saturate a small piece of cotton with ether or ammonia, and place it in a dish. After a short time ask pupils to explain what occurs.

b. Using a thistle tube, half-fill several colorless glass medicine bottles with a 4 percent solution of gelatin. Take care to keep the gelatin from touching the upper part of the bottles. When the gels have set, fill the remaining space of the several bottles with solutions of potassium chromate, cobalt nitrate or of soluble dyes such as magenta. Stopper the bottles. Stand some bottles upright, clamp others upside down, lay some on their sides. Have pupils observe in what directions the color advances.

c. Fill two similar beakers nearly full of water. The water in one should be at room temperature and in the other nearly at the boiling point. Support two thistle tubes upright so that the tubes extend down the center of each beaker to about ⅛ inch from the bottom (see diagram 2.02*c*). Drop a few crystals of potassium permanganate down each tube. Observe the differences in the rate of diffusion.

d. Repeat or review a Brownian movement demonstration (see activity 3.54).



2.02 c

2.03. Historical Development of the Atomic Theory

The study of the development of the theories of atomic structure can be divided into approximately three periods of time.

(1) The period from at least 500 B.C. to about 1800 represented slow, negligible development of a theory mainly on a qualitative basis. The period ended following John Dalton's quantitative work with gases and his statement that indivisible atoms make up matter and that the atoms of any one element are identical to each other but different from atoms of another element. Interested pupils may wish to study the works of Aristotle, Democritus, Lucretius, Boyle, Newton and Dalton (see references *2R-1-3*).

(2) The period from about 1800 to the statement of Niels Bohr's Theory (about 1915) represented a more rapid advance in understanding atomic structures. The principal research tools were the X-ray, the spectroscope and atomic particles. During this time some major discoveries were those of the electron and proton, and also the prediction of the neutron (discovered in 1932). This research culminated in the description of the Bohr-Rutherford atom as consisting essentially of a relatively heavy, positively charged nucleus surrounded by revolving electrons in one or more circular orbits at prescribed distances from the nucleus. This theory was proposed to explain various spectroscopic data.

During this period important discoveries were made or theories were presented by Avogadro, Prout, Mendeleef, Roentgen, Moseley, Planck, Thompson, Chadwick, Rutherford and Bohr. Their work is discussed in most high school textbooks. Additional details may be found in advanced textbooks and in references *2R-4-6*.

(3) The period from 1915 to the present is characterized by an intensive study of the nucleus and by various attempts to explain the probable positions of the electrons. During this period of quantitative study the rate at which theories have been proposed and discoveries have been made has increased exponentially. In addition to the basic research tools of the preceding period, apparatus such as the cloud chamber and accelerators has been especially helpful (see references *2R-7-8*).

2.04. Size of Atoms

The field ion microscope and X-rays are two of the indirect methods used to determine the diameters of atoms. Measurements by various devices indicate that atoms of different elements have different diameters but that the diameter of any atom is approximately 10^{-8} cm.

X-rays and other probes have been used to determine the size and shape of the nuclei and electrons of the atom. These studies indicate that both the nucleus and the electron have a diameter of approximately 10^{-12} cm. These data may be more readily understood by visualizing the hydrogen atom as a golf ball (nucleus) and a ping-pong ball (electron) revolving around the nucleus about 1,000 feet away. It is clear that the atoms consist mostly of "empty" space.

2.05. Use of Probes

The use of analogies may help pupils to understand how probes can be used to give indirect information concerning the size, shape and location of obstructions or vacant spaces in atoms. After the analogies are understood, the pupils should be able to make reasonable conclusions based on hypothetical observations. Some analogies follow.

a. A blind person often uses a cane to determine the location of a wall or an open door. Although not practical, he could also throw tennis balls in each direction. The presence or absence of an obstruction could be determined by the presence or absence of ricochets.

b. Around the edges of a table or desk, place books or any obstruction to prevent objects rolling from the table. In the center of the table, place at different times a sphere of relatively large mass and volume (a billiard ball), a sphere of relatively small mass and volume (a marble or bearing), and a cubical block of wood or another object with a flat surface which can be fixed in place. From various places along the edge of the table, roll similar spheres (marbles and billiard balls) at random across the table. Observe particularly that:

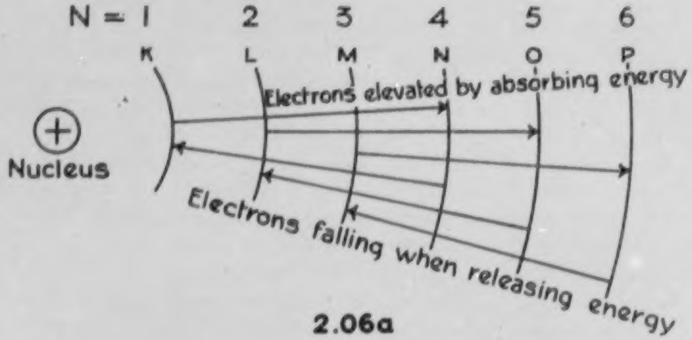
- There are relatively few hits regardless of the size of the obstruction.
- There are relatively few, but more, hits if either the rolled sphere or the obstruction is larger.
- When the obstruction is spherical, the ricochets occur about equally in all directions.
- When the obstruction is a plane surface, the directions of the ricochets are more limited.
- When the small sphere strikes the large sphere, the former rebounds while the latter is hardly affected.
- When the large sphere strikes the small sphere, the motion of the former remains essentially the same while the small sphere is given a large velocity.

2.06. The Bohr Theory

a. **Background Material.** Many attempts have been made to explain how an excited atom radiates energy and why it radiates the particular frequencies that it does. The first acknowledged successful attempt was made by the Danish physicist, Niels Bohr, in 1913.

Bohr stated that an electron could revolve in any one of several orbits about the nucleus while obeying the ordinary laws of mechanics. He suggested that the orbits were concentric circles. These orbits are now denoted by letters *K, L, M, N, O, P* . . . or by numbers *1, 2, 3, 4, 5, 6*. When an electron has been given a certain amount of energy, Bohr indicated it could move to one of the outer circles. Therefore, the orbits represented paths of electrons having increasing energies with the electrons in the innermost orbit having the least energy.

Bohr also stated that the energy radiated by excited atoms was the result of one or more electrons moving from an orbit of higher energy to one of lower energy and that the energy radiated was equal to the difference in the energy possessed by the electrons before and after the moves. Diagram 2.06*a* shows some of the possible moves. He found it necessary to assume that the electron does not gain energy continuously in moving from a lower orbit to a higher one or lose energy continuously when the motion is from higher to lower energy level. He further assumed that the gain or loss of energy was in discrete quantities called *quanta*.


N = 1
2
3
4
5
6
K
L
M
N
O
P
Electrons elevated by absorbing energy
Nucleus
Electrons falling when releasing energy

2.06a

b. Radii of the Bohr Orbits. Pupils adept at handling mathematical computations may be interested in determining the approximate radii of Bohr orbits by using the following formula (see appendix *E-2* for instructions in the use of powers of ten).

$r = \frac{E_0 n^2 h^2}{\pi m e^2}$ where r = radius of a given orbit of hydrogen in meters

n = quantum number of the orbit

h = Planck's constant (6.62×10^{-34} joule-sec.)

m = mass of an electron (9.11×10^{-31} kg.)

e = charge of an electron (1.60×10^{-19} coulomb)

$E_0 = 8.85 \times 10^{-12} \frac{\text{coulomb}^2}{\text{newton-meter}^2}$

For the information of the teacher, the following data indicate the approximate radii of the first three Bohr orbits.

Orbit	Approximate Radius		
n = 1	5.3×10^{-11} m.	$.53 \times 10^{-8}$ cm.	0.53 Å*
n = 2	2.1×10^{-10} m.	2.1×10^{-8} cm.	2.1 Å
n = 3	4.8×10^{-10} m.	4.8×10^{-8} cm.	4.8 Å

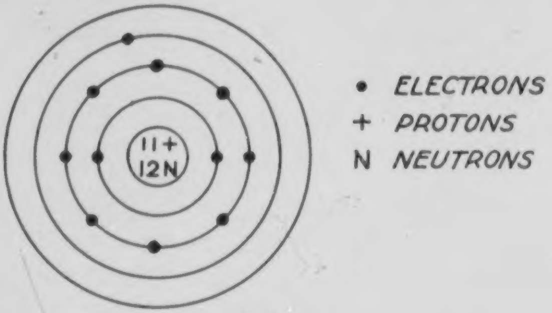
* 10^{-8}cm. = 1 Å

2.07. Demonstration Models of Atomic Structure

For many purposes in elementary chemistry, models of the Bohr-Rutherford atom serve quite well to illustrate atomic number, atomic weight, the principal valences and many chemical combinations of atoms. Stress that the actual atom is three-dimensional and that most of the orbits or orbitals are not circular in shape.

To illustrate the major components of the nuclei of atoms of low atomic number, the individual protons, neutrons and electrons may be represented by colored tacks or colored pegs. As the number of nuclear components increases, the individual components become blurred and can best be represented by writing the totals in the nucleus or on circular pieces of paper which may be attached to the nucleus. However, in the case of most of the atoms to be illustrated, the individual electrons are so separated that they can be seen quite easily. Each device is a modification of diagram 2.07.

a. Draw circles on a large sheet of paper. Paste or fasten the paper on tackboard or heavy cardboard. Use thumbtacks of three colors to represent the particles.



2.07

b. For use with an overhead projector draw circles on a sheet of clear acetate with acetate-type ink (available in art stores). With a paper punch, punch out the particles from pieces of colored acetate or cellophane. Static electricity helps hold the particles in position. The entire set may be conveniently stored in an envelope.

c. Obtain from a builder's supply store a piece of masonite pegboard approximately 4 feet on each side and with holes ½ or 1 inch on center. Using a brush or roller which is practically dry paint each side with a light-colored paint. In the center of the board outline a circle of about a 4-inch radius. Outline four additional evenly spaced concentric rings (1 inch wide) around the center. Paint the inner circle and the 1-inch rings with a contrasting color for easy visibility. The final product resembles a target. Colored wooden pegs (obtained from elementary school supply houses) may be used to represent electrons. *Note:* The other side of this board may be used for exercises described in activities 2.15 and 2.16.

2.08. Pupil Diagrams of Probable Atomic Structure

Pupils will occasionally be required on local and State examinations to represent the probable structure of atoms and ions and to indicate electronic changes which occur during the formation of electrovalent compounds and covalent molecules. Although the pupil should realize that the probable arrangement of the electrons is three-dimensional and rather vague, the two-dimensional diagram is generally satisfactory for elementary explanations and is easier to draw.

In order to prevent misinterpretation due to vague or crowded diagrams, a relatively uniform system of representation should be used. *Although not recommended for this type of explanation*, correctly coded representations of atoms showing subshells of principal energy levels are acceptable. It is suggested that acceptable diagrams include the following features shown in diagram 2.08.

- A title beneath each diagram such as "Sodium Atom"
- The nucleus represented as a circle at least ½ inch in diameter (see diagrams 2.08 *a* and *b*)
- In the nucleus the numbers of protons and neutrons clearly indicated by number and code such as protons (11+ or 11P) and neutrons (12N)
- The completed inner shells represented by dashed arcs or circles about ¼ inch apart with numbers placed on each arc or circle to represent the number of electrons in each completed shell

- The outer (valence) shell represented by a dashed circle with a radius about ¼ inch larger than the radius of the preceding arc and electrons in the valence shell clearly shown as solid circles or by "*e*"
- The formation and structure of ionic compounds with an arrow indicating the shifting of the valence electron to its new position. The shifting electron(s) may be shown as solid circles in the original position and as open circles in the new position. Diagram 2.08*c* represents sodium chloride. Pupils should understand that, in a crystal of sodium chloride, each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions.
- The structure of covalent molecules such as chlorine shown with the chlorine nuclei and inner shells as described above. The valence shells should be dashed circles which intersect at two points with the common area being relatively small. The valence electrons in each atom should be shown as solid circles with the shared electrons being placed on the common area (see diagram 2.08*d*). If the complete structure is not required in the question, only the valence electrons need be shown. For representations of valence electrons only, paired dots shown in many textbooks are also acceptable.

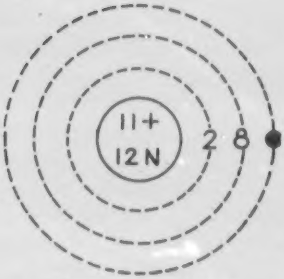
2.09. The Physicist and Atomic Structure

The present theory of the probable structure of the atom has been developed mainly from theories of physicists and the interpretation of spectroscopic data. Details of this progress are available in many advanced textbooks. Teachers or pupils may wish to investigate this topic by using the following highlights in the development of the theory:

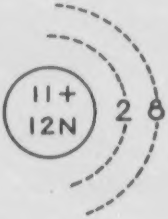
(1) **Planck's Theory and Constant (About 1900).** Planck stated that energy is emitted from or absorbed by a body in certain discrete quantities. The energy is expressed as $E = h\nu$ where h is Planck's Constant and ν is the frequency of radiation. It is obvious that the energy of radiation of high frequency (short wavelength) is greater than that of low frequency (long wavelength).

(2) **Photoelectric Effect.** About 1900 Hertz, Thompson and others demonstrated that light of short wavelength caused the emission of electrons from metals.

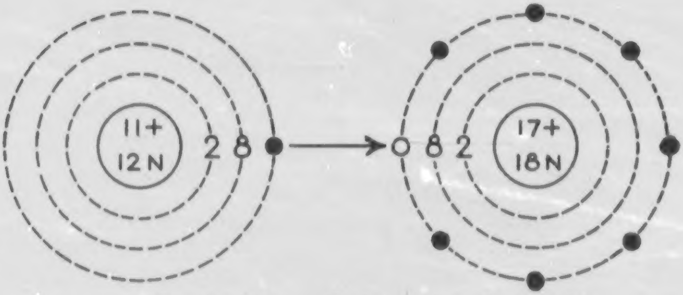
(3) **Einstein's Photoelectric Equation (1905).** Einstein explained the photoelectric effect by mathematical equations. The verification of the equation by Millikan, Compton and others led to general acceptance of the existence of light quanta.



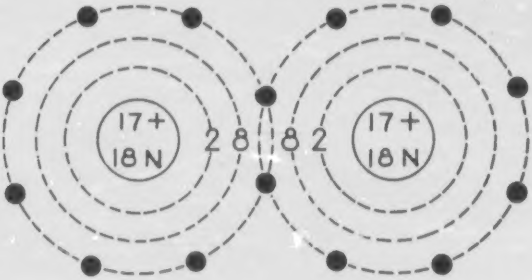
Sodium Atom
a



Sodium Ion
b


11+
12N
2
8
8
2
17+
18N

Formation of Sodium Chloride
c


17+
18N
2
8
8
2
17+
18N

Structure of Chlorine Molecule
d

2.08

(4) **Bohr Theory** (1913). Bohr adapted the theories of quanta stated by his predecessors to his theory of atomic structure. The theory accounted for observed spectroscopic data and predicted additional spectroscopic lines. Their later discovery more firmly established the theory.

(5) **Compton Effect** (1923). Compton used the quantum theory to explain the change in wavelength of some X-rays striking electrons. He stated that X-rays were quanta and that the results of the collisions were similar to those of collisions of two billiard balls. His predicted results were later discovered experimentally and further confirmed the quantum theory.

(6) **Wave-Particle Duality** (1924). Light phenomena can sometimes be explained by assuming that light is composed of waves and, at other times, of particles. De Broglie assumed that forms of matter (such as moving electrons and protons) are also associated with waves.

(7) **Diffraction of Electrons** (1927). Davisson and Germer discovered that electrons were diffracted by crystals as were X-rays, and as described by De Broglie. They concluded that electrons behaved more like waves than particles.

(8) **Wave Equations** (1925-33). De Broglie's work was extended by Schrödinger, Heisenberg and Dirac to an explanation of the wave motion of electrons by complicated mathematical equations. The theory describes certain regions where there is the greatest probability of the electron being located. These equations involve quantum numbers identical with those postulated by Bohr.

(9) **Heisenberg Uncertainty Principle** (1927). This principle states that it is impossible to determine simultaneously the exact position and motion of an object (see reference *2R-9*).

2.10. Photoelectric Effect

a. Cut and bend small "ears" on a 3-inch plate of zinc, so that it can be clipped directly onto the knob of an electroscope. Clean the zinc with sandpaper immediately before using it. Charge the electroscope with the zinc attached, and observe the rate at which the charge leaks off. Illuminate the zinc with light from a carbon arc spotlight, and observe that a positive charge is unaffected but that a negative charge is quickly lost. Since zinc is sensitive to ultraviolet light, the lens must be removed from the arc lamp before this activity is tried. Interpose a piece of glass and observe that the discharge due to illumination ceases, showing the opacity of ordinary glass for ultraviolet. Instead of an arc light an ultraviolet light source (used in a fluorescent mineral demonstration) may be used.

b. The photoelectric effect can be demonstrated by means of an ordinary photographic exposure meter. Some pupils who are interested in photography may have such a meter in their possession. Expose the meter to the varying intensities of light and notice the readings of the meter. Light causes the emission of electrons which comprise the electric current.

2.11. Some Electronic Configurations of the Atom

Bohr's theory was inadequate in that it was able to account for the spectra of only the simplest atoms such as hydrogen. Some spectral lines of heavier atoms could be explained by assuming that electrons had jumped from one of the higher principal energy levels to a lower level. However, additional spectral lines could be explained only by assuming that most principal energy levels were divided into two or more subshells or sublevels, each representing a different energy level. These subshells were named *s, p, d, f, g, h*. The first four letters were chosen as abbreviations of series of spectral lines originally named *sharp, principal, diffuse* and *fundamental*. The remaining letters follow "f" in alphabetical order.

Similar evidence leads to the assumption that each subshell may be further subdivided into one or more orbitals with each orbital having a slightly different orientation. A set of rules can be devised to aid in determining the numbers of principal energy levels, subshells and orbitals, as well as the number of electrons in each. For simple explanations, only the first five rules given below need be used. For more complete explanations replace rule 5 by rules 5*a*, 5*b* and 5*c*.

(1) The total number of electrons outside the nucleus equals the number of protons in the nucleus (*atomic number*).

(2) The maximum number of electrons for each principal energy level (n) equals $2n^2$. The maximum number of electrons in the outermost shell is limited to eight and the next outermost shell to 18.

(3) The number of possible subshells for each principal energy level (n) equals n.

(4) The subshells are designated *s, p, d, f, g, h*.

(5) The maximum number of electrons for each subshell is 2 electrons for "s," 6 electrons for "p," 10 electrons for "d," 14 electrons for "f" and so on.

(5*a*) The "s" subshell has one orbital; the "p" has three; the "d" has five; the "f" has seven, and so on.

(5*b*) The total number of orbitals for each principal energy level is n^2.

(5*c*) An orbital can hold no more than two electrons.

2.12. Pupil Diagrams Representing Electronic Configurations

Teachers usually prefer to illustrate the electronic configurations for several elements by aid of some visual devices before giving pupils the opportunity to practice the same manipulations. If relatively simple explanations are desired, only the first 18 elements should be used for practice.

Depending upon the degree of complexity desired, at least three types of configurations may be shown. In each of the following three cases chlorine is used as an example. Each step in a possible presentation is explained by reference to a specific rule mentioned in activity 2.11.

(1) Use of Principal Energy Levels Only

A chlorine atom has 17 electrons outside the nucleus *(rule 1)*.

The first energy level (n = 1) has two electrons *(rule 2)*.

The second energy level (n = 2) has eight electrons *(rule 2)*.

The third energy level (n = 3) could have only eight electrons *(rule 2)*, but has only seven electrons *(rule 1)*.

Summarize the arrangements of the electrons for chlorine in some manner such as shown for sodium in diagram 2.08*a*.

(2) Use of Principal Energy Levels and Subshells Only

Chlorine has 17 electrons outside the nucleus *(rule 1)*.

The first principal energy level (n = 1) has two electrons *(rule 2)*. There is only one subshell *(rule 3)* which is designated "s" *(rule 4)*. This subshell has two electrons *(rule 5)*.

The second principal energy level (n = 2) has eight electrons *(rule 2)*. There are two subshells *(rule 3)* designated "s" and "p" *(rule 4)*. The "s" and "p" subshells contain two and six electrons respectively *(rule 5)*.

The third principal energy level (n = 3) may contain only eight electrons *(rule 2)*. There are three possible subshells *(rule 3)* designated "s," "p" and "d" *(rule 4)*. For chlorine only seven electrons appear in the third energy level *(rule 1)*. The "s" and "p" subshells contain two and five electrons respectively. The "d" subshell exists but has no electrons.

This information for each subshell may be summarized in a shorthand notation such as $1s^2$. The *s* indicates the type of subshell; the coefficient *1* indicates the principal energy level; the exponent or superscript *2* indicates the number of electrons in each subshell. Summarize by use of this notation the electronic configuration for a chlorine atom as $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^5$.

(3) Use of Principal Energy Levels, Subshells and Orbitals

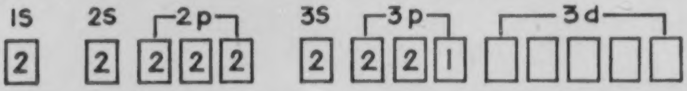
In this approach rules 5*a*, 5*b* and 5*c* are substituted for rule 5. The same type of reasoning is used as in the preceding case. In addition, it can be shown that for chlorine:

For n = 1 there is one orbital *(rule 5b)*. The "s" subshell has one orbital *(rule 5a)* with two electrons *(rule 5c)*.

For n = 2, there are four orbitals *(rule 5b)*. The "s" subshell has one orbital *(rule 5a)*; the "p" subshell has three orbitals *(rule 5a)*; each orbital has two electrons *(rule 5c)*.

For n = 3, there are nine possible orbitals *(rule 5a)*. The "s" subshell has one orbital *(rule 5a)* of two electrons *(rule 5c)*. The "p" subshell has three orbitals *(rule 5a)*. In the "p" subshell two of the orbitals have two electrons *(rule 5c)*, while the third has only one *(rule 1)*.

Show the electronic configuration for a chlorine atom by boxes to indicate the orbitals with electrons in each orbital, such as:



Note: The empty "3d" orbitals have been included although not used.

Indicate similar information for the first 18 elements by one or all of the preceding methods. Stop the discussion of subshells at element number 18 unless prepared to discuss peculiarities which are noted for several elements including potassium (see activity 2.13). Summarize this information in chart form, such as shown on page 60.

2.13. "Unusual" Electronic Configurations

Refer to the theory of atomic structure discussed in activity 2.12. Note that electrons tend to fill the principal energy levels and subshells having the lowest energy level first and then to fill progressively those subshells of higher energy. The electrons which are on the average closer to the nucleus are associated with a lower energy level. For example, in argon which is represented by $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, the energy of each subshell increases as one moves from left to right. One would expect that if the subshells were listed in order of increasing energy, they would appear as: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 3*d*, 4*s*, 4*p*, 4*d*, 4*f*, 5*s*, 5*p*, 5*d*, 5*f*, 5*g*, 6*s*, 6*p*, and so on. However, evidence indicates that the order of subshells is: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*. Note that an "unusual" configuration occurs at several places, such as 4*s* preceding 3*d* and 5*s* preceding 4*d*. Obviously the

Element	Atomic Number	Electrons In Principal Levels (Shells) K	L	M	Electrons In Principal Levels And Subshells
Hydrogen	1	1			$1s^1$
Helium	2	2			$1s^2$
Lithium	3	2	1		$1s^2$, $2s^1$
Beryllium	4	2	2		$1s^2$, $2s^2$
Boron	5	2	3		$1s^2$, $2s^2$, $2p^1$
Carbon	6	2	4		$1s^2$, $2s^2$, $2p^2$
Nitrogen	7	2	5		$1s^2$, $2s^2$, $2p^3$
Oxygen	8	2	6		$1s^2$, $2s^2$, $2p^4$
Fluorine	9	2	7		$1s^2$, $2s^2$, $2p^5$
Neon	10	2	8		$1s^2$, $2s^2$, $2p^6$
Sodium	11	2	8	1	$1s^2$, $2s^2$, $2p^6$, $3s^1$
Magnesium	12	2	8	2	$1s^2$, $2s^2$, $2p^6$, $3s^2$
Aluminum	13	2	8	3	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$
Silicon	14	2	8	4	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^2$
Phosphorus	15	2	8	5	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$
Sulfur	16	2	8	6	$1s^2$, $2s^2$. $2p^6$, $3s^2$, $3p^4$
Chlorine	17	2	8	7	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^5$
Argon	18	2	8	8	$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$

average probable location of the electrons in the 4*s* orbital is closer to the nucleus than the average probable location of the electrons in the 3*d* orbital. This and other apparent discrepancies are accounted for by some orbitals having greater eccentricity than others (see activity 2.14 under orbital quantum number).

2.14. Quantum Numbers

As more spectral lines were observed in spectroscopes of higher resolving power, the quantum theory was revised to explain the additional lines. It is now believed that four items of information are required to describe accurately the energy and most probable location of any electron of an atom. This information is found in the four quantum numbers:

(1) **Principal Quantum Number.** This number (n) denotes the major axis of the orbit of an electron and represents the *size of the electron orbit.* The first principal energy level (n = 1) is the same as the first *K* shell or level. Numbers *2, 3, 4* represent the *L, M* and *N* shells, and so on.

(2) **Azimuthal (Orbital) Quantum Number.** The number *l* denotes the angular momentum of the electron in its orbit. This number indicates the ellipticity of the orbit or the *shape of the orbit.* For any principal energy level the value of *l* ranges from zero to (n — 1). When n = 4, there are four subshells designated $l = 0$, $l = 1$, $l = 2$, $l = 3$. These *l* values refer to *s, p, d* and *f* orbitals respectively. (See activity 2.11, *rules 3* and *4.*)

In this case, the largest value of *l* ($l = 3$) represents the most circular path (4*f* orbital), while the smallest value of *l* ($l = 0$) represents the most elliptical path 4*s* orbital. An exception occurs in the 1*s* subshell where the only orbital ($l = 0$) is circular.

For a given energy level, electrons in the most elliptical orbital *(s)* may approach closest to the nucleus. These electrons have the lowest energy. In some cases, the ellipticity of an orbital is so great that this orbital penetrates the orbital of a lower principal energy level. An example is the 4*s* orbital penetrating the 3*d* orbital which results in an "unusual" electronic configuration (see activity 2.13).

The *l* number can be used to determine the permissible jumps of electrons between energy levels to produce spectral lines. The *l* values of the *s, p, d* and *f* sublevels are 0, 1, 2 and 3 respectively. In any single jump, the *l* value must change by only +1 or —1. For example, a jump between an *s* orbital and a *p* orbital is possible while a jump between an *s* orbital and a *d* orbital is not allowed.

(3) **Magnetic Quantum Number.** The number *(m)* describes

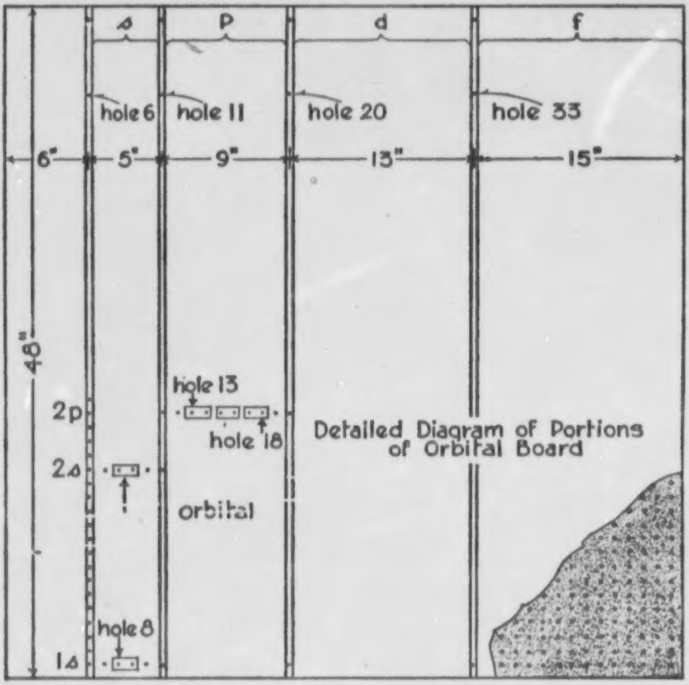
how an orbit is oriented in space. It was postulated to account for the splitting of spectral lines by a magnetic field.

(4) Spin Quantum Number. The number *(s)* describes how an electron spins on its axis while moving in its orbit. If compared to a rotating sphere when viewed from above, the motions may be considered clockwise and counterclockwise. A pair of electrons with opposite spins may be represented by two arrows placed side by side, one pointing up and the other pointing down.

By use of these four quantum numbers, an electron may be identified. The Pauli exclusion principle states that no two electrons in an atom may have *all* four quantum numbers the same, that is, have the same energy (see reference *2R-10*).

2.15. Demonstration Orbital Board

As a pupil project, a demonstration orbital board may be constructed of masonite pegboard approximately 4 feet on each side and


s
p
d
f
hole 6
hole 11
hole 20
hole 33
6"
5"
9"
13"
15"
48"
hole 13
2p
hole 18
2s
orbital
hole 8
1s
Detailed Diagram of Portions of Orbital Board

2.15

with holes ½ inch or 1 inch on center. The reverse side of the board used in activity 2.07*c* is suitable. Although few teachers will discuss more than 10 orbitals, details for additional orbitals have been included for possible future use. If only 10 orbitals are shown on the entire board, the same ratios of distances between energy levels should be maintained.

The vertical axis of the completed board is approximately a scaled representation of the relative energy levels of the electrons from the "1s" sublevel to the "6*p*" sublevel. Along the left vertical side identify the subshells either by painting on the board or sticking strips of marked tape on the board. The approximate location of each sublevel is opposite the number of the hole given in the following chart starting from the bottom. Opposite the number of each sublevel are boxes to represent the number of orbitals in each of the "*s*," "*p*," "*d*" and "*f*" sublevels. Each orbital (box) is two holes wide in order to hold two electrons (pegs) of different spin. See diagram 2.15 illustrating this arrangement.

SUBLEVEL	HOLES FROM BOTTOM (48-HOLE BOARD)	HOLES FROM BOTTOM (96-HOLE BOARD)	NUMBER OF ORBITALS (BOXES)
6p	45	91	3
5d	44	89	5
4f	43	87	7
6s	42	85	1
5p	40	80	3
4d	39	77	5
5s	38	74	1
4p	35	68	3
3d	33	65	5
4s	32	63	1
3p	28	55	3
3s	25	48	1
2p	19	36	3
2s	15	28	1
1s	1 (lowest)	1 (lowest)	1

The board is further divided into columns representing the four possible sublevels. Paint four vertical strips ¼ inch wide on the board. (Masking tape, colored cellulose tape or adhesive tape are also suitable.) On a 48-hole board the four vertical strips can cover horizontal holes numbered *6*, *11*, *20* and *33*. Paint (or mark with tapes) the orbital boxes as rectangles approximately 1¾ inches long and ¼ inch wide. Each orbital box should have its base on the proper sublevel line and should cover two holes. Keep a narrow space between each orbital for easy identification.

2.16. Representing Electronic Configuration on the Orbital Board

The orbital board described in activity 2.15 may be used as an extension of activity 2.11. Two purposes of this extension may be to lead into a discussion of the periodic table or to introduce pupils to this topic which they will study in further detail in advanced chemistry courses. Electrons of different spin are represented by red and green pegs (available in elementary school supply houses).

In addition to the rules given in activity 2.11, these additional rules are required:

(1) An orbital holds no more than two electrons, each of a different spin.
(2) An electron enters the lowest energy level available.
(3) Two electrons will not enter an orbital until there is at least one electron in each orbital of that subshell.

Illustrate the electronic configurations of the first 36 elements by use of red and green pegs. The information given in the following chart will aid in determining the way in which the electrons of different spin enter the orbitals. Except for the limitations of *rule 3* above, either type of electron (shown by *R* and *G*) can enter any orbital in a given subshell first. The order shown in the diagram has been selected arbitrarily for convenience. If elements in period 4 are illustrated, note the exceptions in elements 24 and 29 for which no simple explanation can be given. The probable electronic configurations of additional elements are given in many advanced chemistry textbooks and in chemistry handbooks.

2.17. Spectral Lines

The necessity to explain spectral lines led to modifications in the theory of atomic structure. Pupils can observe some of these spectral lines. The observing apparatus required is a spectroscope or an inex-

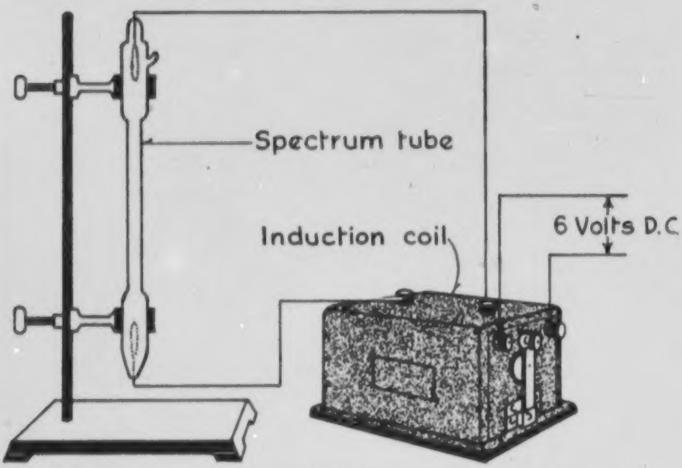
PERIOD	ELEMENT	Z	$1s^2$	$2s^2$	$2p^6$	$3s^2$	$3p^6$	$4s^2$	$3d^{10}$	$4p^6$
1	H	1	R							
	He	2	RG							
2	Li	3	Same as Helium	R						
	Be	4		RG						
	B	5		RG	R					
	C	6		RG	R R					
	N	7		RG	R R R					
	O	8		RG	RGR R					
	F	9		RG	RGRGR					
	Ne	10		RG	RGRGRG					
3	Na	11	Same as Neon			R				
	Mg	12				RG				
	Al	13				RG	R			
	Si	14				RG	R R			
	P	15				RG	R R R			
	S	16				RG	RGR R			
	Cl	17				RG	RGRGR			
	Ar	18				RG	RGRGRG			
4	K	19	Same as Argon					R		
	Ca	20						RG		
	Sc	21						RG	R	
	Ti	22						RG	R R	
	V	23						RG	R R R	
	Cr	24						R	R R R R R	*Exception
	Mn	25						RG	R R R R R	
	Fe	26						RG	RGR R R R	
	Co	27						RG	RGRGR R R	
	Ni	28						RG	RGRGRGR R	
	Cu	29						R	RGRGRGRGRG	*Exception
	Zn	30						RG	RGRGRGRGRG	
	Ga	31						RG	RGRGRGRGRG	R
	Ge	32						RG	RGRGRGRGRG	R R
	As	33						RG	RGRGRGRGRG	R R R
	Se	34						RG	RGRGRGRGRG	RGR R
	Br	35						RG	RGRGRGRGRG	RGRGR
	Kr	36						RG	RGRGRGRGRG	RGRGRG

pensive plastic replica grating (obtained from most scientific supply houses). Hold the latter before the eyes in a darkened room.

a. Clean a platinum wire by dipping it in hydrochloric acid. Dip the wire in a solution of NaCl. Hold the wire in the nonluminous flame of a bunsen burner and observe the intense yellow line. Other lines may also be seen. Repeat with solutions of LiCl and $Sr(NO_3)_2$.

b. Soak asbestos in a solution of NaCl. Wrap the wet asbestos around the barrel of a bunsen burner so that the upper edge of the asbestos will be in contact with the flame when the gas is ignited. Repeat with different salt solutions. Compare the colors and locations of the lines.

c. Connect a spectrum tube containing hydrogen to the terminals of an induction coil (see diagram 2.17*c*). Observe the location of the lines.

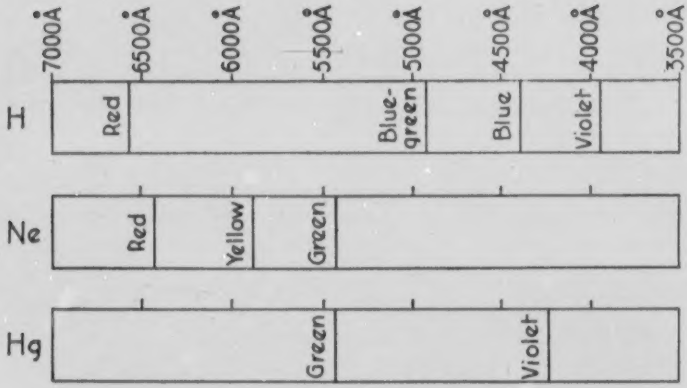


2.17 c

d. Repeat the above using tubes of neon and mercury. Use diagram 2.17*d* to compare the locations of the strongest visible lines in the spectra of hydrogen, neon and mercury.

2.18. Historical Background of the Periodic Table

Point out that, as more elements were discovered, it became necessary to classify them for ready study. Although all classifications take into account certain similarities, the earlier classifications were based upon



2.17 d

atomic weights, while later ones were based on atomic numbers. Based on the early tables some predictions of properties of the elements later discovered have been remarkably accurate. The highlights and approximate dates in this historical development of classification are:

- Dobereiner (1817 and 1829). "*Triads.*" In certain groups of three similar elements such as calcium, strontium and barium, the atomic weight of the second element is approximately equal to the *mean* of the atomic weights of the other two.
- Newlands (1865). "*Law of Octaves.*" If elements are arranged in order of increasing atomic weights, there are many cases where chemical properties are repeated for every eighth element.
- Meyer (1865-70). "*Atomic Weights.*" A table was established based upon atomic weights, which also indicated that certain physical properties are periodic functions of some elements.
- Mendeleef (1869). "*Atomic Weights.*" A table was prepared similar to that of Meyer, which was more widely accepted. Note the similarity of predicted properties of ekasilicon and actual properties of germanium.
- Moseley (1913). "*Atomic Numbers.*" By use of X-rays, it was established that the properties of elements were periodic functions of the atomic numbers. This modification cleared up many inconsistencies in Mendeleef's table.

An excellent reference book for this and related topics is given in the bibliography, ***Fundamental Concepts of Inorganic Chemistry.***

2.19. Forms of the Periodic Table

The chemistry classroom and laboratory should feature well-located, readable periodic tables that can be referred to constantly during the course. It is desirable to display both the short or "folded" form and the more popular long form. A chart indicating the relative sizes of atoms and ions in the periodic table is very useful.

Note that the following changes in symbols were made recently in order to avoid confusion with certain symbols in physics, mathematics and nuclear science:

- Argon, formerly *A*, now *Ar*
- Einsteinium, formerly *E*, now *Es*
- Mendelevium, formerly *Mv*, now *Md*

The table is not a "foundation" of chemistry. Its value lies mainly in its *usefulness* to pupils and chemists. The usefulness is more important than the "defects of the table." A description of the discovery of "Freons" will illustrate this point.

Pupils should be trained to refer to the tables frequently, especially through the example of the teacher. The periodic table included in *Reference Tables for Chemistry* should be made available for practice frequently during the course. It is good practice to permit use of a table during most quizzes. Introduction of the table early in the course is desirable. However, it is advantageous to postpone treatment of the "*B*" groups until later.

Show the pupils that by folding the table between Groups *2A* and *3B*, and again between *2B* and *3A*, the B group can be folded back out of sight and the more regular *A* groups consolidated. Point out to the pupils that some forms of the periodic table make a different division of Groups *A* and *B*.

2.20. The Periodic Arrangement—Based upon Electronic Configuration

Illustrate the similarities in electronic configurations of the elements in the various groups by reference to the Periodic Table of the Elements shown on pages 334-335, or to either activities 2.12 or 2.16. As an aid to the teacher, the major groups are described briefly to indicate electronic dissimilarities of the principal energy levels. For a more detailed treatment refer to an advanced inorganic textbook.

(1) **First Type.** Elements in Group *O*. The electronic stability of these elements cannot be improved by electron transfer or by electron sharing. All "*s*" and "*p*" sublevels are complete. These elements do not ordinarily react.

(2) **Second Type.** Elements in Groups *IA, IIA, IIIA, IVA, VA, VIA* and *VIIA*. Elements of this type tend to lend, borrow or share electrons so that their outermost shells will resemble those in Group *O*. All inner shells are complete while the outer shell is incomplete. The most common or "representative" elements are included in these groups.

(3) **Third Type.** Elements in Groups *IIIB, IVB, VB, VIB, VIIB* and *VIIIB*. (*IB, IIB*). Elements of this type exhibit variable valence and are called transition elements. They are characterized by having the two outermost shells incomplete. This distinguishing characteristic does not apply to Groups *IB* and *IIB*, since they have electronic structures similar to type *II* elements. However, the elements in Group *IB* and *IIB* are included here because their chemical behavior is most similar to the chemical behavior of the other "*B*" group elements. *Note:* The electron structures of some transition elements are in doubt and will be predicted differently in various references.

(4) **Fourth Type.** Elements of the lanthanide series (element numbers 58-71) and of the actinide series (element numbers 90-102). These represent other types of transition elements, differing from regular transition elements by having three outermost shells incomplete instead of two.

The traditional name for the lanthanide series, "rare earth elements," no longer has any particular merit, and its use should not be encouraged. The term "radioactive rare earths" for the actinide series is erroneous. Thorium and uranium are "common" rather than "rare."

2.21. Generalizations Based on the Periodic Table

The elements in the Periodic Table of the Elements shown on pages 334-335 are arranged according to atomic number and electronic configuration. Differences in chemical properties of the elements are related largely to: (1) the magnitude of the nuclear charge, (2) the number of shells and the number of electrons in the shells and (3) the distances of the electrons from each other and from the nucleus. To a less obvious extent, differences in physical properties may be accounted for in a similar manner.

A study of the periodic table leads to many generalizations, including those listed below. Some of these generalizations can best be illustrated and explained concurrently with the study of the periodic table, while others may more easily be illustrated at other times. *Concepts that are essentially identical are frequently stated in several ways.* In some instances areas of the course or specific activities have been related to a generalization.

(1) Elements in the periodic table are arranged according to their atomic numbers.

(2) For any element in a period, the number of principal energy levels equals the period number.

(3) The atomic number increases from left to right and from top to bottom.

(4) The atomic weight generally increases from top to bottom and from left to right.

(5) The number of neutrons in an atom of an element generally increases from left to right and from top to bottom.

(6) As the mass number increases from 1 to approximately 60, the stability of the nuclei increases; above 60 the stability generally decreases.

(7) Hydrogen exhibits both metallic and nonmetallic properties, and is often an exception to any generalization about its location on the table.

(8) Elements to the left of the heavy line running stepwise from boron to astatine are generally classed as metals.

(9) Elements to the right of the heavy line running stepwise from boron to astatine are generally classed as nonmetals.

(10) Elements that border the heavy line running stepwise from boron to astatine exhibit intermediate properties and are known as metalloids (aluminum sometimes excepted).

(11) Metals greatly outnumber nonmetals.

(12) Elements in Group *IA* are known as the alkali metals.

(13) Elements in Group *IIA* are known as the alkaline earths.

(14) Elements in Group *VIIA* are known as the halogens.

(15) Elements in Group *O* are known as the noble elements or the inert gases.

(16) Groups other than *IA*, *IIA*, *VIIA* and *O* are often known by the name of a common element in the group; for example, oxygen group for *VIA*.

(17) Metals conduct heat better than nonmetals.

(18) Metals are better conductors of electricity than nonmetals (exception carbon).

(19) The boiling points of metals are generally higher than those of nonmetals.

(20) Some metals of high density and low melting point are those with atomic number of *30-33*, *48-51* and *80-83*.

(21) Some metals of high density and high melting point are those in Groups *IVB, VB, VIB, VIIB, VIIIB* and *IB*.

(22) Metals of low density are found in the upper part of the table in Groups *IA, IIA* and *IIIA*.

(23) Elements tend to form ions by borrowing or lending electrons to produce the electronic configuration of the inert element closest in atomic number.

(24) Positive ions are appreciably smaller than their corresponding atoms; negative ions are appreciably larger than their corresponding atoms.

(25) Ions of elements in Group *IA* have smaller ionic radii than negative ions of the *same* electronic configuration.

(26) Metals tend to lose electrons more easily than nonmetals; nonmetals tend to gain electrons more easily than metals.

(27) Metals have small ionization potentials; nonmetals have large ionization potentials.

(28) Elements which have large differences in electronegativity (such as those in Groups *IA* and *VIIA*) form ionic compounds; those which have small differences of electronegativity tend to to form compounds which are primarily covalent.

(29) Electrovalent (ionic) compounds are generally solids with high melting points.

(30) Covalent compounds are generally gases, or liquids with low boiling points.

(31) In each group, as the atomic number increases in the group, the radius of the atom increases (more pronounced in the "representative" elements).

(32) In Groups *IA, IIA, VIA* and *VIIA* particularly, as the atomic number increases in the group the elements become less electronegative (more electropositive).

(33) Elements in Group *IA* have a valence of 1 and an oxidation state of +1 in their compounds.

(34) Elements in Group *IIA* have a valence of 2 and an oxidation state of +2 in their compounds.

(35) Elements in Group *VIIA* have a valence of 1 and an oxidation state of —1 in binary compounds.

(36) The transitional elements (the *B* groups) tend to have more than one valence and more than one oxidation state.

(37) Those elements which do *not* attain the electronic configuration of the inert elements when they form ions generally have multiple valences.

(38) In all *A* groups, as the atomic number increases in the group, the elements tend to have more metallic properties.

(39) In Group *IA* as the atomic number increases, the density of the element generally increases. (Relate to metals.)

(40) In Group *IA* as the atomic number increases, the melting point and the boiling point of the element decrease.

(41) In Group *IA* and in Group *IIA*, as the atomic number increases in the group, the hardness of the element decreases.

(42) Elements on the left side of the table (metals) lose electrons in forming compounds.

(43) In Group *IA* and in Group *IIA*, as the atomic number increases in the group, the tendency of the element to lose the valence electron(s) increases.

(44) In Group *IA* and in Group *IIA*, as the atomic number increases in the group, the chemical activity of the element increases.

(45) In Group *IA* as the atomic number increases, the reducing ability of the element increases.

(46) In Group *VIIA* and in Group *O*, as the atomic number increases in the group, the boiling point of the element increases.

(47) In Group *VIIA*, as the atomic number increases, the melting point of the element increases.

(48) In Group *VIIA*, as the atomic number increases, the density of the element increases.

(49) In Group *VIIA*, as the atomic number increases, the oxidizing ability of the element decreases.

(50) In Group *VIIA*, as the atomic number increases, the strength of the binary acid increases.

(51) In Group *VIIA*, as the atomic number increases, the color of the element deepens.

(52) Elements on the right side of the table (nonmetals) tend to gain electrons in forming compounds.

(53) In Group *VIA* and in Group *VIIA*, as the atomic number increases in the group, the tendency of the element to gain electrons decreases.

(54) In Group *VIA* and Group *VIIA*, as the atomic number increases in the group, the chemical activity of the element decreases.

(55) In Groups *O* and all *A* groups, as the atomic number increases in each group, the ionization potential decreases. (More pronounced in Groups *IA*, *IIA* and *O*.)

(56) The most active metals are found in the lower left-hand corner of the table; the most active nonmetals are found in the upper right-hand corner of the table (disregard Group *O*).

(57) In Groups *IA*, *IIA*, *VIA*, and *VIIA*, as the atomic number increases in the group, the radius of the ion increases. (Due to multiple valences, the sizes of ions vary in other *A* and *B* groups.)

(58) In each period, as the atomic number increases in the period, the radius of the atom generally decreases.

(59) In each period, as the atomic number increases in the period, the ionization potential of the element generally increases.

(60) In each period, as the atomic number increases in the period, the elements generally change from very active metals, to less active metals, to metalloids, to less active nonmetals, to very active nonmetals.

(61) As the periodic chart is observed from left to right, a tendency for the elements to form strong bases, weak bases, amphoteric hydroxides, weak binary acids and strong binary acids, in that order, becomes apparent.

(62) As the periodic chart is observed from left to right, there is a transition from positive to negative oxidation numbers. Elements near the center of the table may exhibit both positive and negative oxidation numbers.

(63) In each period, as the atomic number increases in the period, the metallic characteristics of the *A* group elements decreases.

(64) In each period, as the atomic number increases in the period, the electronegativity of the element increases.

2.22. Activities Based on the Periodic Table

Many generalizations summarized in activity 2.21 may be verified from data available in well-known reference books. This type of activity serves to give the pupil experience in the use of reference materials, a skill required in advanced sciences. Two excellent sources are *Handbook of Chemistry and Physics*, published by the Chemical Rubber Publishing Company, and *Handbook of Chemistry* by N. A. Lange, published by Handbook Publishers, Inc.

If desired, data may be obtained for elements other than those suggested in this and in the preceding activity. The explanations of various interesting exceptions to the generalizations may be beyond the scope of an introductory course.

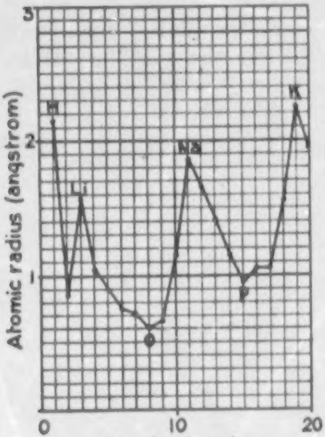
Many of the obvious activities require constant reference to the periodic table. Trace on a master duplicating ditto sheet pertinent portions (squares, atomic numbers, period and group numbers) of the Periodic Table of the Elements distributed for use with Regents examinations. (A copy appears on pages 334-335.) Reproduce in sufficient quantity to allow each pupil enough copies to record on separate sheets various data (some of these data may also be plotted as illustrated in diagrams 2.22*a*, *b*, *c* and *d*), such as:

(1) The boiling points of elements by group, period or both (note particularly Groups *IA*, *IIA*, *VIIA* and *O*). (See activity 2.21, generalizations 19, 40 and 46.)

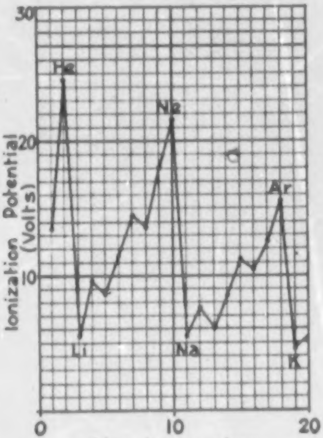
(2) The melting point of elements by group, period or both. (See activity 2.21, generalizations 20, 21, 40 and 47.)

(3) The density of elements by group, period or both. (See activity 2.21, generalizations 20, 21, 22, 39 and 48.)

(4) The atomic radii of the elements (refer to Lange under "Atoms, effective radii of"). Note that data from various sources differ slightly. (See activity 2.21, generalizations 24, 31 and 58; also, diagram 2.22*a*.)

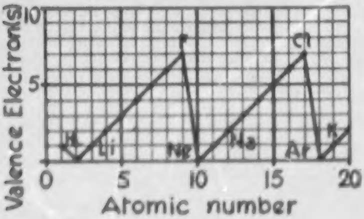


2.22a

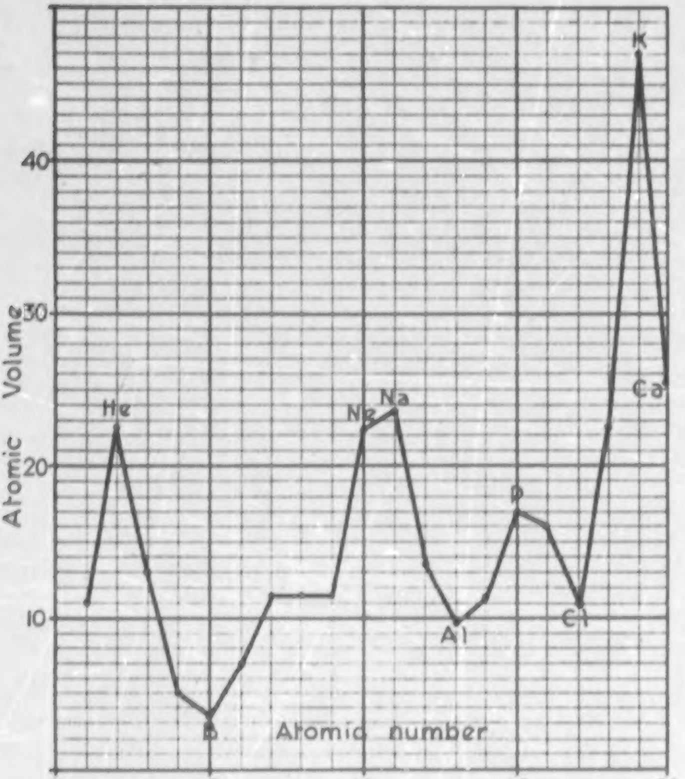


2.22b

(5) The ionic radii of the elements (refer to Campbell's *Chart of Relative Sizes of Atoms and Ions in the Periodic Table* or to Lange as above). Note that data from various sources differ slightly. (See activity 2.21, generalizations 24, 25 and 57.)


Valence Electron(s)
10
5
0
5
10
15
20
Atomic number
H
Li
F
Ne
Na
Cl
Ar
K

222c


Atomic Volume
40
30
20
10
0
5
10
15
20
He
Ne
Na
Al
P
Cl
K
Ca
B
Atomic number

2.22d

(6) The first ionization potentials of the elements by group, period or both. (See activity 2.21, generalizations 27, 55 and 59; also, see diagram 2.22*b*.)

(7) The electronegativities of the elements (exclude the transition elements). (See activity 2.21, generalizations 28, 32 and 64.) (Refer to the bibliography.)

(8) The melting points of a representative sample of ionic compounds. (See activity 2.21, generalization 29.)

(9) The boiling points of a representative sample of covalent compounds. (See activity 2.21, generalization 30.)

(10) The number of valence electrons for the elements with atomic numbers 1 through 20. (See diagram 2.22*c*.)

(11) The atomic volume of the number of elements with atomic numbers 1 through 20. (See diagram 2.22*d*.)

2.23. Determining Atomic Weights

As usually considered, atomic weight is a relative weight in comparison to the weight of some arbitrary standard. Currently, there are at least three arbitrary definitions of atomic weight:

- *Chemical atomic weight*—based on 16.00000 units as the average weight of a natural mixture of the isotopes of oxygen.
- *Physical atomic weight*—based upon the 16.00000 units as the atomic weight of O^{16}.
- *Mass number* (used mainly by nuclear scientists)—based upon the sum of nucleons, each with a mass of one unit.

There is a strong possibility that a new basis may be adopted for uniformity and greater precision. Two possibilities are the masses of F^{19} and C^{12}.

No balance is sensitive enough to weigh an atom. Determinations of the weight of an individual atom are based upon Avogadro's number, 6.02×10^{23} which is the number of atoms in a gram atom of a substance or the number of molecules in a gram-molecular weight of a gas. The latter weight occupies 22.4 liters at S.T.P.

To appreciate the small weight of an atom and to practice the use of powers of 10 and significant figures, pupils may compute the weight of atoms of various gases (see appendix *E*). Hydrogen is given as an example:

Gram-molecular weight of hydrogen gas = 2.00 gm.

Number of molecules in this volume of hydrogen = 6.02×10^{23}

Weight of one molecule of hydrogen $= \dfrac{2.00 \text{ grams}}{6.02 \times 10^{23}} = 3.32 \times 10^{-24}$ gm.

Each molecule has two atoms.

Therefore, the weight of each hydrogen atom is 1.66×10^{-24} gm.

2.24. Computing the Average Atomic Weight of an Element

The average atomic weight of an element, as given in the Periodic Table of the Elements (see pages 334-335), is the average of the weights of the atoms in a naturally occurring mixture of the isotopes of the element, if any. Computation of some of these average weights by pupils is an interesting mathematical extension which leads to an understanding of the process. Although advanced textbooks give details for further refinement of the method, the following example is sufficiently accurate to illustrate the principle:

Data in the various chemical handbooks indicate that the occurrences of the principal isotopes of magnesium are:

Mg^{24}—78.6 percent of atomic mass 23.9924

Mg^{25}—10.1 percent of atomic mass 24.9938

Mg^{26}—11.3 percent of atomic mass 25.9898

It is obvious that the average atomic mass (chemical atomic weight) is between 24 and 26 and closer to 24. The weighted average is computed as:

$$\begin{aligned} Mg^{24} &= 23.9924 \times .786 = 18.86 \\ Mg^{25} &= 24.9938 \times .101 = 2.52 \\ Mg^{26} &= 25.9898 \times .113 = \underline{2.94} \\ & 24.32 \end{aligned}$$

This corresponds to the weight given in the table. Compute the average atomic weights of additional elements.

Area 2. References

2R-1. Ancient ideas in modern chemistry. Journal of Chemical Education, v. 29, No. 8: 386. Aug. 1952

2R-2. Antecedents to the Boyle concept of the elements. Journal of Chemical Education, v. 33, No. 11: 548. Nov. 1956

2R-3. John Dalton's "autobiography." Journal of Chemical Education, v. 32, No. 6: 333. June 1955

2R-4. Prout's hypothesis. Journal of Chemical Education, v. 33, No. 6: 33. June 1956

2R-5. The nineteenth century atom: undivided or indivisible? Journal of Chemical Education, v. 36, No. 2: 64. Feb. 1959

2R-6. Elementary particles. Scientific American, v. 197, No. 1: 72. July 1957

2R-7. Anti-matter. Scientific American, v. 198, No. 4: 34-39. April 1958

2R-8. The weak interactions. Scientific American, v. 200, No. 3: 72-84. Mar. 1959

2R-9. The principle of uncertainty. Scientific American, v. 198, No. 1: 51. Jan. 1958

2R-10. The exclusion principle. Scientific American, v. 201, No. 1: 74-86. July 1956

NOTES

AREA 3

Solutions and Near Solutions

3.01. The Nature of Solutions

A solution is a homogeneous mixture of two or more substances, the composition of which may be varied. The dissolving medium is the *solvent* and the substance dissolved is the *solute.*

Prepare two containers of water of suitable size which can readily be seen. To the first add a spoonful of clean sand, sulfur or a granulated metal, and stir. To the second add a spoonful of a colorful powdered compound such as copper nitrate, ammonium dichromate or nickel sulfate, and stir. Contrast the contents of the two containers. Discuss the "disappearance" of the colored salt, the "appearance" of color (chromogens) in every drop of the second container, the homogeneous distribution of the color and the permanent (nonsettling) character of the mixture. Compare the solution with a spoonful of the dry salt in a beaker and encourage the pupils to explain what must have taken place among the molecules of solvent and solute to account for the difference.

To assist the discussion make a solution in "slow-motion" as follows: By means of a burning candle, place a daub of wax on the bottom (convex) surface of a watchglass or petri dish, and push into the wax a crystal of potassium permanganate. Float the dish on a large cylinder filled to the brim with water. Observe the process of dissolving.

3.02. Rate of Solution

The rate of solution is controlled by such factors as surface area, agitation and temperature. Demonstrate the effect of each to the class.

a. Surface Area. Weigh a large crystal of copper sulfate, chrome alum, rock candy, rochelle salt or similar material. With a mortar and pestle finely pulverize an equal weight of the same material. Add the two portions to separate beakers containing equal amounts of water. Stir the contents of the two beakers at equal rates. Since all other conditions are equal, the degree of subdivision must be responsible for the different rates of solution. Explain that here, *rate* means the quantity dissolving per unit of time.

Display an apple, orange or potato and discuss the amount of exposed surface. Bisect with a knife and point out the increase in surface. Make several more cuts to show that the greater the degree of subdivision the larger the surface exposed to the environment.

b. Agitation. Pulverize a small quantity of a colorful soluble salt such as copper sulfate. Divide this into two equal portions by weight. Add one portion to a beaker of still water. Add the other to a beaker set up for rapid agitation of the contents with a magnetic stirrer, electric "blender" or by hand. Show that in the first case a heavy, locally saturated solution soon surrounds the crystals if left undisturbed, while in the second case agitation constantly brings unsaturated solvent in contact with the crystal surfaces. Repeat, but, instead of agitating in the second beaker, tie the salt in an empty tea bag and suspend just under the surface. The heavier saturated solution can now flow downward, and fresh solvent moves constantly into the bag, effecting a faster rate of solution. Indicate that the process of going into solution occurs only on the surface of the solid.

c. Temperature. Select two small crystals of potassium permanganate of about equal size. Prepare two beakers containing equal amounts of water, one at room temperature or colder, the other at about 80°C. Drop a crystal in each, and observe the rates of solution. Relate this to the increased molecular activity at the surface of the crystal and increase in the rates of diffusion. Raise the question of the effect of convectional currents in the solvent on the rate of solution.

3.03. Filterability of Solutions

Before defining "true solution," point out that, besides true solutions, certain colloidal solutions are apparently homogeneous and not separable by filtration. In general, true solutions contain particles which are less than one millimicron (10^{-6} mm.) in diameter. Whether a solution is colloidal or not may be partly determined by particle size and partly upon how the solution originated. For example, certain colloids may be formed by an electric arc or controlled precipitation.

Display "rapid" filter paper for coarse precipitates and "dense" filter paper for fine precipitates. Point out that in order to separate a mixture by filtration the particles of solvent and "solute" must differ in size, and the filtering medium (paper, cloth or powders) must have openings that will allow only one component to pass. Show that ordinary filtering mediums cannot remove the solute from a solution of copper sulfate by pouring some through a dense filter paper and comparing the filtrate with some of the original solution. Open the filter paper. Emphasize that this is not a test for true solutions, because a number of colloids behave in the same way. Point out that scientists have developed special membranes whose pores are so small that they are capable of filtering certain solutes from true solutions.

3.04. Varieties of Solutions

After defining solution, solvent and solute, have the pupils complete a review chart similar to the one illustrated below.

SOLUTE	SOLVENT	EXAMPLE
Solid	Solid	
Solid		Salt in water
	Gas	Sulfur vapor in air
Liquid	Liquid	
Liquid		Mercury in copper
Liquid	Gas	
Gas	Gas	
	Liquid	Soda water
Gas	Solid	

3.05. Insolubility

In the strictest sense, no substance is absolutely insoluble.

Grind up and finely powder a 1-foot length of soft glass tubing (6 mm.) with a mortar and pestle. Use a glove or towel to protect your hand from tiny glass splinters. Pour the powdered glass into a bottle half filled with distilled water and stopper. Shake the bottle thoroughly for several minutes or heat the mixture. Remove the stopper and add 5 drops of phenolphthalein indicator. The faint pink color indicates the presence of sodium silicate in solution. The "solubility" of glass in water accounts for the storage of very pure water in containers of pure quartz and of distilled water in tin-lined copper drums.

3.06. Factors Governing Solubility

Illustrate the rough principle that "like dissolves in like" by setting up test tubes for the following solvents: water (covalent polar), carbon tetrachloride (covalent nonpolar), and ethyl alcohol (molecules polar on one end, nonpolar on other). Add some pellets of sodium hydroxide (ionic compound) to each, and note that it is very soluble in water, less soluble in ethanol, and practically insoluble in carbon tetrachloride, Repeat, using fresh solvents, and study the solubility of kerosene (covalent nonpolar). Emphasize that solubilities are by no means strictly predictable and scientists still work them out largely by trial and error.

3.07. Cosolvency

Show that some substances dissolve best in a blend of solvents. Shake 1 gm. of sodium oleate powder (a soap-type molecule) with 5 ml. of propylene glycol in one tube and 1 gm. of the same powder with 5 ml. of chloroform in another. The powder will not dissolve completely in either solvent. Now pour the two together and shake. The sodium oleate immediately goes into solution. This property is called "cosolvency."

03.08. Solutions and Crystal Forces

Shake some sodium chloride on a metal pan which has been strongly heated over a bunsen burner. To explain why it does not melt, refer to a handbook to find the exact melting point of the salt. Relate this to the strength of the bonds in the crystal lattice.

Dissolve some NaCl in water, and note the relative ease with which the solution process takes place. Melting requires sufficient heat energy to overcome the bonding forces which hold the crystal together. One of the main reasons why the dissolving of NaCl in water takes place more readily is because energy is *released* when ions of Na^+ and Cl^- interact with the polar H_2O molecules. This energy is commonly known as the hydration energy. Although forces holding the crystal together must be overcome also in the solution process, the extra hydration energy is available to help solution in water.

3.09. Mechanism of Dissolution

a. Ionic Solutes. With cutouts to represent the ions and polar water molecules, use a felt board, magnetic blackboard or overhead projector to illustrate the manner by which ions are pulled off the dissolving crystal by electrostatic attraction. Point out that these solvent molecules remain loosely attached to the ion forming a "hydration ion," whose rate of diffusion and rate of migration toward electrodes are slowed down.

b. Covalent Solutes. Use a similar arrangement to that in *a* above to illustrate the dissolving of a lump of sugar in water. The sugar molecules are more attracted to the water molecules than to each other.

A possible explanation is that the hydrogen bonds between sugar and water molecules are stronger than the forces bonding sugar molecules in a sugar crystal. The fact that the forces binding covalent molecules into crystals are weak is revealed by their relatively low melting points. Refer to the melting points of naphthalene, urea and camphor. Hydrogen bonding plays an important role in holding protein molecules in solution, as in the case of egg albumin in egg white. Whipping or cooking the egg white disrupts the hydrogen bonds and results in precipitation.

3.10. Variations in Solubility

a. New Ionic Species. Prepare test tubes half-full of each of the following: water, ethyl alcohol, carbon tetrachloride and a 10 percent solution of potassium iodide in water. Add a few crystals of iodine to each (molecules are covalent and nonpolar) and shake the test tubes. Ask the class to suggest why the iodine is only sparingly soluble in water, somewhat more soluble than alcohol, and extremely soluble in carbon tetrachloride. Heat a few crystals of iodine in a dry 1-liter Erlenmeyer flask and show the color relation between iodine gas and iodine dissolved in carbon tetrachloride or other organic solvents. Point out that dissolved substances are in many respects in a "gaseous" condition. Iodine is more soluble in solutions of potassium iodide than in pure water due to the formation of a new ionic species:

$$I_2 + K^+ + I^- \rightarrow K^+ + (I_3)^-$$

Tincture of iodine commonly contains alcohol, water and potassium iodide in order to dissolve more iodine.

b. Preferred Solvents. To illustrate variations in solubility, form layers by mixing 25 ml. of carbon tetrachloride, 25 ml. of water and 25 ml. of ether. Add a few crystals of iodine. A similar demonstration consists of carbon tetrachloride, glycerol and amyl acetate to which is added a crystal of methyl red. Carbon disulfide, water and nitropropane may also be used with methyl red as the solute.

3.11. Solubility Through Complex Ion Formation

Formation of "complex ions" frequently plays a great role in solubility. To a test tube half-filled with water add a pinch of sodium chloride and dissolve. Add a few ml. of 10 percent silver nitrate solution to form the highly insoluble white precipitate of silver chloride. Write the equation. Add an excess of concentrated ammonia water to the test tube. Stir until the precipitate "dissolves." This is due to the chemical interaction between the precipitate and the dissolved ammonia gas to form a "complex ion" which is soluble:

$$AgCl + 2NH_3 \rightarrow Ag(NH_3)_2^+ + Cl^-$$

Many other examples may be found in any text on qualitative analysis.

3.12. Depression of Solubility with Mixed Solvents

Finely powder 50 gm. of copper sulfate. The probable structure of each of these ions is: $Cu(H_2O)_4^{++}$ and $SO_4(H_2O)^{--}$. Mix with 50 ml. of water until no more appears to go into solution. Add a few drops of concentrated ammonia water and note the whitish precipitate of copper (II) hydride. Now add 75 ml. of concentrated ammonia water and stir thoroughly. The precipitate dissolves and a clear solution with a deep blue color results. A deep blue soluble complex ion forms similar to the tetraquocopper (II) ion, $Cu(H_2O)_4^{++}$, except that the four water molecules have been replaced by four ammonia molecules. This new ion, $Cu(NH_3)_4^{++}$, is called the tetraamminecopper (II) ion.

While vigorously stirring the solution, drop into it very slowly from a dropping funnel 75 ml. of ethyl alcohol. Deep purple-blue crystals of $Cu(NH_3)_4SO_4 \cdot H_2O$ precipitate from the solution. Recover the crystals from the solution by filtration. The addition of alcohol is a common device to bring about the crystallization of metallic salts which cannot be obtained by evaporation due to the possibility of decomposition.

The preparation of $Cu(NH_3)_4SO_4 \cdot H_2O$ makes an excellent project for advanced students. Begin with the preparation of anhydrous copper sulfate from copper metal and concentrated sulfuric acid. *CAUTION: Use hood for this reaction.* Crystallize the hydrated form and proceed as indicated above. The final crystals should be collected by suction filtration. After pressing free of mother liquor, dry in a desiccator over lime.

3.13. Chelation

Another case related to inducing solubility by complex formation is an important new technique in chemistry—the use of "chelates." These are organic compounds capable of "encircling" and holding an ion in solution under conditions that would otherwise cause it to precipitate. The most famous of these compounds is *EDTA* (ethylene-diamine-tetra-acetic acid or its salts). A student volunteer should write to chemical manufacturers (addresses available through advertising in *Chemical and Engineering News*, see appendix *F*), and report to the class on the interesting applications of this technique. Another student might prepare some demonstrations for the class (see reference *3R-1*).

3.14. Limitation of Solubility

The solubility of gases in gases is unlimited provided they are chemically inert toward each other. Miscible liquids, molten metals and salts have a similar unlimited solubility in each other. Some alloys (solid solutions) can be prepared in unlimited proportions. The most common type of solution, solids in liquids, is typically limited.

Place 100 ml. of distilled water in each of four beakers. Heat the water in three of the beakers to 60°C and the water in the fourth to 30°C. To the first beaker add 0.02 gm. of calcium sulfate, to the second 37.3 gm. of sodium chloride, to the third 110 gm. of potassium nitrate and to the fourth 219.5 gm. of table sugar. Point out that in two cases the solute outweighs the solvent. Add more of the same solid to each solution to show that it will not dissolve.

A convincing demonstration that equilibrium truly exists may be easily given. A corner is broken from an otherwise perfectly formed crystal and the crystal is then suspended in a solution saturated with respect to this same solute. Over a long period of time the imperfection in the crystal is repaired. It ultimately becomes a perfectly formed crystal again, though slightly smaller over all, because the total quantity of solute in the solvent remains unchanged. This result can be achieved only through dynamic equilibrium.

3.15. Effect of Temperature on the Solubility of Solids

In general, solids are more soluble at higher temperatures.

a. To 100 gm. of potassium nitrate in a beaker add 100 ml. of distilled water. Stir until no further solution seems to take place. Observe the temperature. Determine the weight of the salt now in solution by referring to solubility tables. Predict how hot the solution would have to be to dissolve all the salt. While stirring frequently, heat the solution to the selected temperature. Place a little of the warm solution in a petri dish and allow it to cool on the stage of the overhead projector.

b. Shake a small amount of lead chloride with cold water in a test tube. Heat the water, boiling if necessary, until the salt dissolves. Lower the temperature by holding the tube under the cold water tap.

3.16. Negative Temperature Effects

Some salts become less soluble as the temperature rises. Dissolve 0.2 gm. of pure calcium hydroxide (be sure it has not converted to $CaCO_3$) in 200 ml. of water and heat to boiling, or saturate 100 ml. of ice water (0°C) with 19 gm. of ferric sulfate and raise to boiling.

Have the class explain the results by reference to the solubilities of these substances as listed in a handbook. Also try calcium acetate and calcium chromate.

3.17. Solubility Curves

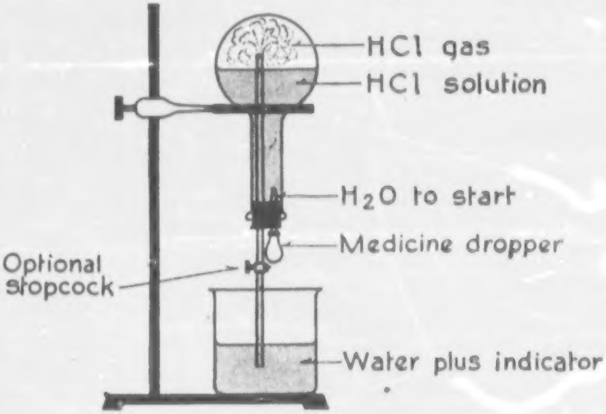
Have the class construct a solubility curve for potassium bromide or ammonium chloride by assigning different temperatures to each individual and plotting the points as submitted on a chalkboard graph. Capable students should be encouraged to try others; for example, the solubility curve for sulfur in benzene. Allow 24 hours for the solution of sulfur to become saturated at each temperature. See also Manufacturing Chemists Association, *Scientific Experiments in Chemistry*, "Making a Solubility Curve," and reference *3R-2*.

3.18. Heat of Solution

To separate beakers containing about 100 ml. of water slowly add a small quantity of concentrated sulfuric acid, sodium hydroxide, concentrated nitric acid, hydrogen chloride gas, ammonium nitrate, hypo and urea. Stir with a thermometer and note any temperature changes. Interested pupils may wish to determine how this effect is used in "solar houses."

3.19. The Solubility of Gases in Liquids

Place two tall cylinders of water side by side. Drop a piece of dry ice into one. If dry ice is not available, blow through a glass tube that



3.19

extends to the bottom, or use compressed air. To the second cylinder admit bubbles of ammonia gas from a tank or generator. Account for the changing volumes of the bubbles as they rise in the water.

CAUTION: Danger of implosion. Demonstrate the hydrogen chloride or ammonia fountain. See diagram 3.19. Be sure to use a sound, unscratched, round bottom pyrex flask, not more than 2 liters in capacity. For best effect, do a thorough job of expelling all the air from the flask with the gas chosen. Place the flask as shown and squeeze the medicine dropper to start the fountain. The solution in the beaker should include an appropriate indicator; phenolphthalein for the ammonia setup, brom thymol blue plus one drop of ammonia water for the hydrogen chloride variation.

3.20. Effect of Pressure on the Solubility of Gases

Show that a 7-oz. bottle of soda water contains not just the gas visible above the liquid, but a "glass of gas." Open a bottle of soda water (previously well warmed under the hot water faucet) under an inverted 7-oz. glass full of warm water in a pneumatic trough.

3.21. Effect of Temperature on the Solubility of Gases

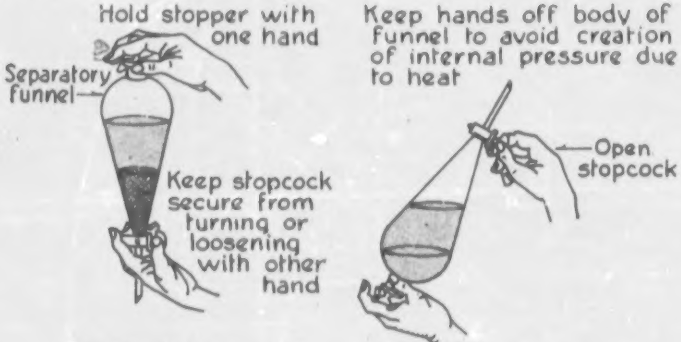
Place a few drops of ammonia water in a beaker of water and add a drop of phenolphthalein (or thymolphthalein) indicator. Boil the solution and note the color change. Add another drop of indicator to show that ammonia has left the solution. Place a bottle of soda pop in an ice-salt bath, chill and open. Allow a second bottle to remain open at room temperature during the period. At the end of the period pour the contents of both into two glasses. The amount of foam is a rough approximation of the amount of dissolved gas. See reference *3R-3.*

3.22. Miscible Liquids

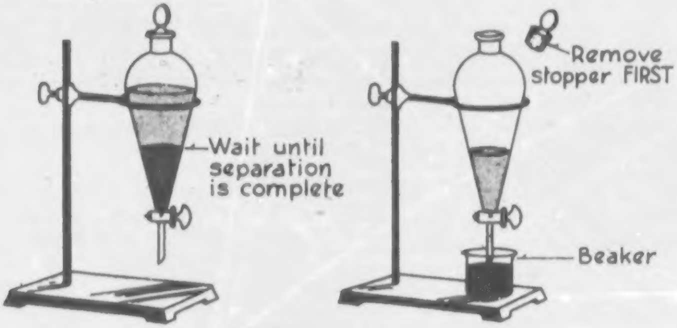
To a 100-ml. volumetric flask add exactly 50 ml. of water, and exactly 50 ml. of ethanol. Note the final volume. Add this solution to more alcohol or water to show miscibility. An interesting result is obtained by adding 50 ml. of carbon disulfide to 50 ml. of ethyl acetate.

3.23. Partially Miscible Liquids

Into a 500-ml. separatory funnel introduce 250 ml. of water and 100 ml. of ether. Shake the mixture according to the technique shown in diagram 3.23. Allow to settle, and show the two layers. Some saturated copper sulfate solution added to the funnel will make the lower water layer more distinct. Separate the layers into two beakers. Show that water has dissolved in ether to some degree by adding a little anhydrous copper sulfate to the ether. After removing all ether to a safe distance, pour the water layer into a shallow pan and *carefully* throw a lighted match onto its surface.


Hold stopper with one hand
Separatory funnel
Keep stopcock secure from turning or loosening with other hand
Keep hands off body of funnel to avoid creation of internal pressure due to heat
Open stopcock

1. Shaking 2. Relieving pressure


Wait until separation is complete
Remove stopper FIRST
Beaker

3. Settling 4. Separation of lower layer

3.25

3.24. Immiscible Liquids

Even though some liquids are described as immiscible practically all liquids can dissolve at least traces of others.

a. Dissolve a small particle of some oil-soluble dye; for example, oil red, in 50 ml. of carbon disulfide. Dissolve a little water soluble dye of another color in 50 ml. of water; for example, congo red plus one drop of any acid. Add the two liquids to a large test tube and shake.

b. To a glass cylinder or test tube add equal amounts of the following liquids: mercury, carbon tetrachloride (or carbon disulfide), water and gasoline (or light oil or ether). To highlight the differences in density of the liquids, add the following objects: cork, oakwood (or other dense wood), an egg, a copper or silver coin, a piece of gold or platinum. The five objects will take up positions at the five surfaces.

3.25. Types of Solution—Degree of Concentration

Exhibit several colorless solutions of different concentrations. Show that visual inspection reveals nothing about their concentration and that clear, neat labels are important. Set up six large test tubes of water in a rack and add increasing amounts of potassium permanganate, or a similar colored substance to each tube. Shake until the contents of each tube are completely dissolved. Use only a few crystals in the first, many in the last, so that the colors will range from very faint pink to almost black. Point out that the eye can now detect the differences in concentration. Prepare another test tube with a degree of color such that it will be intermediate to two of the original series. Ask the class to identify where it should be inserted in the rack to maintain an increasing concentration relationship among the tubes. Point out that if the concentration of the original six were exactly known, the upper and lower limits of the concentration of this "unknown" could be established. Ask the class to outline a rapid method for evaluating ores for their manganese content.

Dilute a colored solution with water until the color as seen from the side of the test tube is not readily discernible. Pour this solution into a long narrow tube and show that by looking down through the long column toward a sheet of white paper the color is still apparent. Compare with a similar tube filled with plain water. This is the principle of Nessler tubes and the DuBosq colorimeter.

Modern electric colorimeters replace the human eye with a photocell. Point out the wide application of this technique in chemical analysis. Visual or electric colorimeters are easy to construct and make excellent projects for students (see references *3R-4-5*).

3.26. Standard Solutions

Any solution whose concentration is known is called a *standard solution*. Normal and molar solutions are the most common examples of standard solutions.

a. General Techniques of Cleaning Glassware. Before preparing any standard solution, the glassware to be used should be washed thoroughly with a laboratory detergent, rinsed with tap water, and then rinsed several times with small amounts of distilled or deionized water. The water drains off clean glassware without leaving drops sticking to the glass. Watchglasses and pipettes must be allowed to drain dry before use. Other glassware, such as beakers and volumetric flasks, can be used while damp.

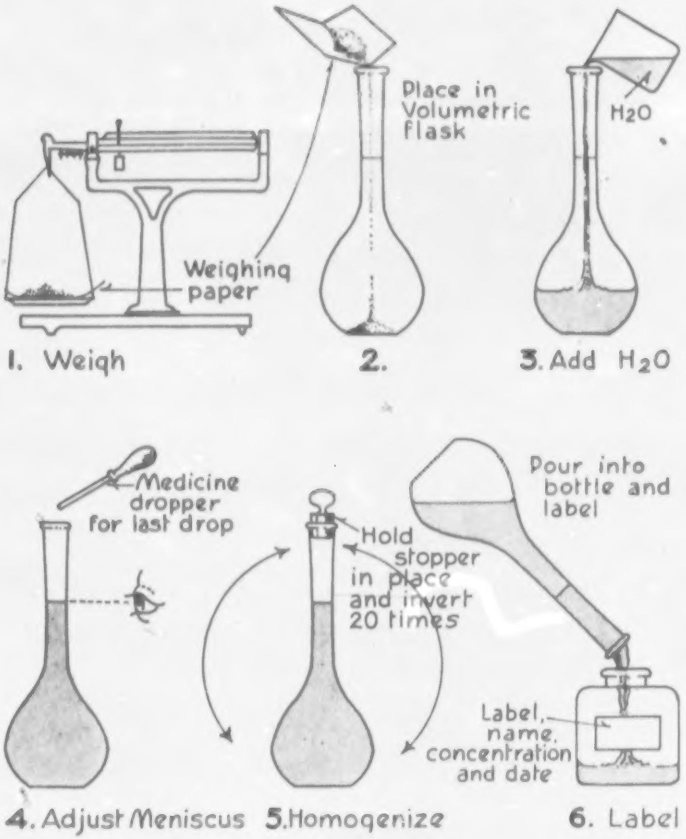
b. Preparation with a Solid Solute. If a solid solute is to be used in making a standard solution, first weigh a watchglass. Add the solute to the watchglass until the combined weight of watchglass and desired weight of solute is reached. Put about 300 ml. of water in a 600-ml. beaker. Transfer the solute to the beaker by washing the solid off the watchglass and into the beaker. Stir. When all the solute has been dissolved (add more water if necessary), transfer the solution to a liter volumetric flask. With a wash bottle squirt a few milliliters of deionized water around the side of the beaker. Put the rinse water into the flask. Rinse the beaker and stirring rod several more times, each time adding the rinse water to the solution. Pour distilled or deionized water into the flask until the bottom of the meniscus of the solution reaches the liter mark on the neck of the flask. Holding the stopper in place, invert the flask several times to mix the contents. Transfer the solution to a labeled stock bottle. The last step is important when the standard solution contains a solute such as sodium hydroxide. The solution can "freeze" the ground glass stopper to the volumetric flask. Diagram 3.26 represents an alternate method which may be used.

C. Preparation with a Liquid Solute. If a liquid solute is to be used in making a standard solution, it is more convenient to measure volume rather than weight of liquid. First it is necessary to calculate the volume of solute needed.

Look up the specific gravity or density of the liquid. The information can be found in reference tables in chemical handbooks and sometimes is printed on the label of the bottle of liquids such as concentrated acids. Specific gravity can be converted to density by multiplying the specific gravity (*sp. gr.*) by 1 gm./ml. Use the density formula, $D = \frac{\text{weight}}{\text{volume}}$ to calculate the required volume of solute.

Measure the volume of the liquid solute with graduated pipettes or burettes so that tenths of a milliliter can be obtained.

Pour a few hundred milliliters of water into a beaker. While stirring, slowly add the desired volume of solute. Transfer the solution to a liter volumetric flask. Follow the same rinsing procedure and volume adjustments listed in *b* above.


Place in
Volumetric
flask
H2O
Weighing
paper
1. Weigh
2.
3. Add H_2O
Medicine
dropper
for last drop
Hold
stopper
in place
and invert
20 times
Pour into
bottle and
label
Label,
name,
concentration
and date
4. Adjust Meniscus
5. Homogenize
6. Label

3.26

3.27. Molar Solutions

a. Definition. A one molar (1M) solution contains one mole or gram-molecular weight of solute per liter of solution. Likewise, a 0.1M solution contains 0.1 gram-molecular weight of solute per liter of solution. By the use of proportions, calculate the weight of solute needed to make any volume of a known molarity. Follow the general procedures in activity 3.26 when using the calculated weight of solute to prepare the solution.

b. Mathematical Applications.

(1) *Prepare a 0.500M solution of sucrose* ($C_{12}H_{22}O_{11}$).

A 1M solution contains one mole (one gram-molecular weight) of solute per liter of solution.

One mole of $C_{12}H_{22}O_{11}$ = 342.3 gm.

0.500 mole of $C_{12}H_{22}O_{11}$ = 0.500 x 342.3 gm.

$= 1.71 \times 10^2$ gm. = 171 gm.

Add to a volumetric flask 171 gm. of sucrose and enough water to make exactly one liter of solution.

(2) *Prepare a 1.00M solution of sulfuric acid.*

A 1.00M solution contains one mole of solute per liter of solution.

One mole of H_2SO_4 = 98.0 gm.

Assume commercial sulfuric acid (sp. gr. 1.84) contains 95.0 percent acid by weight.

$$\text{Commercial acid needed} = \frac{98.0 \text{ gm.}}{0.950} = 1.03 \times 10^2 \text{ gm.} = 103 \text{ gm.}$$

Add about 500 ml. of water to the volumetric flask first. Carefully add 103 gm. of commercial H_2SO_4; mix constantly. Cool the outside. Care should be taken in adding the acid.

(3) *Determine the molarity of a solution containing 23.1 gm. of ethyl alcohol* (C_2H_5OH) *in 200 ml. of solution.*

Molecular weight of C_2H_5OH = 46.1

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\dfrac{23.1 \text{ gm.}}{46.1 \text{ gm./mole}}}{0.200 \text{ l.}}$$

$$= 2.50 \frac{\text{mole}}{\text{l.}} = 2.50 \text{ M}$$

3.28. Formal Solutions

a. Definition. When referring to substances which either do not exist as molecules or for which the molecular weight is not known, it is more correct to use the expression "formula weight" rather than "molecular weight." When "formula weight" is used the concentration is expressed in "formality" (*F*) rather than in "molarity." A one-formal solution is a solution that contains one formula weight of solute per liter of solution.

b. Mathematical Applications.

(1) *Prepare a 2.0F solution of $NaNO_3$.*

Formula weight of $NaNO_3 = 85$

Two formula weights of $NaNO_3 = 1.7 \times 10^2 = 170$

Add to a volumetric flask 170 gm. of $NaNO_3$ and enough water to make exactly one liter of solution.

(2) *What weight of $KClO_3$ is required to prepare 300 ml. of F/4 (0.250 formal) solution?*

Formula weight of $KClO_3 = 123$

$$\frac{0.250 \text{ gram-formula wt.}}{\text{l.}} \times \frac{123 \text{ gm.}}{\text{gram-formula wt.}} \times 0.300 \text{ l.}$$

$= 9.22$ gm.

Add 9.22 gm. to water to make 300 ml. of solution.

(3) *If 25 ml. of 5.0F $AgNO_3$ are diluted to a volume of 300 ml. by adding water, what is the formality of the diluted $AgNO_3$?*

The number of formula weights in 25 ml. of 5.0F $AgNO_3$ =

$$0.025 \text{ l.} \times 5.0 \, \frac{\text{formula-wt.}}{\text{l.}} = 0.12 \text{ formula-wt.}$$

$$\text{Formality after dilution} = \frac{0.12 \text{ formula-wt.}}{0.30 \text{ l.}}$$

$$= 0.40 \, \frac{\text{formula-wt.}}{\text{l.}}$$

$$= 0.40 \text{ F}$$

3.29. Normal Solutions

a. Definition and Preparation. A one-normal (1N) solution contains one gram-equivalent weight of solute per liter of solution. The gram-equivalent weight of a material is that weight which can combine with or replace one gram (one gram-atomic weight) of hydrogen.

From the formula of a solute the number of equivalents can be found easily. Each positive charge on the cation(s) present can combine with or replace one gram of hydrogen or its equivalent. Therefore, the total positive charge of the solute cation(s) indicates the number of hydrogen equivalents. For example, in the formula $Al_2(SO_4)_3$, there are a total of 2(+3) or 6 positive charges for aluminum ions. Six hydrogen ions can be replaced. The equivalent number for aluminum sulfate is 6.

To calculate the gram-equivalent weight of solute needed to make one liter of 1-normal solution, simply divide the gram-molecular weight of the solute by its number of equivalents. For example, divide the gram-molecular weight of aluminum sulfate by 6 to get its gram-equivalent weight.

Follow the general procedures listed in activity 3.26 in preparing the solution.

If a normality other than 1N is desired, calculate the amount of solute needed to make 1N and then use a proportion to calculate the amount of solute needed for the required normality.

When carrying out reactions, it is advantageous to use normal solutions since equal volumes of the same normalities will give exact combining weights.

b. Mathematical Applications.

(1) *Prepare 1.0N solution of hydrochloric acid.*

A 1N solution contains one gram-equivalent weight of solute per liter of solution.

Gram-equivalent weight of HCl = gram-formula weight = 36.5 gm.

Assume commercial hydrochloric acid (sp. gr. 1.19) contains 38 percent acid by weight.

$$\text{Commercial acid needed} = \frac{36.5\text{ gm.}}{.38} = 96\text{ gm.}$$

Place 96 gm. of commercial HCl in a volumetric flask and then add enough water to make exactly one liter of solution.

(2) *What weight of $Ca(OH)_2$ is required to prepare 150 ml. of 0.01N solution?*

The hydrogen equivalent of $Ca(OH)_2$ is 2.

Equivalent weight of $Ca(OH)_2$ = ½ x formula weight
= 0.50 x 74 = 37.

Weight required = normality x volume x equivalent weight

$$= \frac{0.01\text{ gm-equiv. wt.}}{\text{l.}} \times 0.15\text{ l.} \times \frac{37\text{ gm.}}{\text{gm.-equiv. wt.}}$$

$$= 0.06\text{ gm.}$$

(3) *What volume of water is required to dilute 20 ml. of 0.40N sulfuric acid to a concentration of 0.01N?*

The amount of pure acid in 20 ml. of 0.40N H_2SO_4 = 0.020 l. $\times\ 0.40\ \frac{\text{gm.-equiv.}}{\text{l.}}$ = 0.0080 gm.-equiv.

$$\text{Volume of solution after dilution} = \frac{0.0080\text{ gm.-equiv.}}{0.10\text{ gm.-equiv. l.}}$$

$$= 0.080\text{ l.}$$

$$= 80\text{ ml.}$$

The volume of water required for the dilution equals the final volume minus the original volume.

The volume required = 60 ml.

This problem may also be solved by using the method shown in activity 3.32 *a*.

3.30. Molal Solutions

a. Definition. One gram-molecular weight of solute is used per 1,000 grams of solvent in making a one-molal solution. This method of expressing concentration is used when volumetric flasks are not available for use in making molar or normal solutions. Molal solutions are used to determine molecular weights by freezing point depression.

b. Mathematical Applications.

(1) *Prepare a 1.00m solution of glycerine* $C_3H_5(OH)_3$.

1 mole of $C_3H_5(OH)_3$ = 92.1 gm.

Add 92.1 gm. of glycerine to 1,000 gm. of water.

(2) *A solution of sucrose* ($C_{12}H_{22}O_{11}$) *in water is 1.71 molal. How many grams of sucrose are dissolved in 800 gm. of water?*

$$\text{Moles in water} = 0.800 \text{ kg.} \times 1.71 \frac{\text{moles}}{\text{kg.}} = 1.37 \text{ moles.}$$

One mole of sucrose = 342.3 gm.

The solution contains $1.37 \text{ mole} \times 342.3 \frac{\text{gm.}}{\text{mole}}$

or 469 gm. of sucrose.

3.31. Percent Solutions

a. Definition. The concentration of a solution is sometimes expressed in parts of solute per 100 parts of solution. A 40 percent solution contains 40 grams of solute per 100 grams of solution. Since for all practical purposes each milliliter of water weighs one gram at laboratory temperatures, one can say the 40 percent solution can be made by dissolving 40 grams of solute in 60 ml. (60 gm.) of water.

b. Mathematical Applications.

How many grams of a 6.0 percent solution of NaCl are necessary to yield 4.5 gm. of NaCl?

Six grams of NaCl are contained in 100 gm. of solution.

One gram of NaCl is contained in $\frac{100}{6.0}$ gm. of solution.

$$\text{Weight of solution needed} = \frac{100}{6.0} \text{ gm.} \times 4.5 = 75 \text{ gm.}$$

3.32. Diluting Standard Solutions

a. Procedure. Any normal solution can be diluted to another normality of lower value. Use the relationship:

volume desired × normality desired = volume standard × normality standard.

For example, assume that 100 ml. of a 0.10N solution is desired and a 1.0N solution is available.

100 ml. x 0.10N = 1.0N x volume standard

10 ml. = volume of 1.0N to be used.

In a 100-ml. volumetric flask, pour a few ml. of distilled water. With a graduated pipette, transfer 10 ml. of the 1.0N standard to the flask. Bring the volume up to 100 ml. by adding water. Stopper the flask, while firmly holding the stopper in place, tip the flask back and forth so the contents of the flask can become uniformly mixed.

Molar solutions can be diluted in a similar manner. Use the relationship volume desired × the molarity desired = volume standard × molarity standard.

3.33. Comparing Densities

To prepare a solution dense enough to float marbles, measure 15 ml. of pure water into a dish from a pipette or burette. Add 65 gm. of potassium iodide and 75 gm. of mercuric iodide to the water and stir continuously until the red solid dissolves completely. Upon filtering, a saturated solution of 30 ml. of K_2HgI_4 with a density of 3.19 gm. per ml. at 23°C. is obtained. Put the solution in a small clear pill bottle with a plastic top, and provide a neat label. Float a marble (density about 2.6 gm. per ml.) in the liquid. To prevent deterioration of the solution, keep it tightly stoppered, and protect from light when not in use by wrapping the bottle in aluminum foil.

3.34. Stereoisomers

Certain solutions, notably sugars, have the property of rotating the plane of polarized light. Certain molecules called stereoisomers (mirror images) exist in right-handed and left-handed arrangements, and cause rotation of the light in equal amounts, but in opposite directions. Simple instruments called polarimeters (not to be confused with polarographs) can be made to identify and measure this property using inexpensive Polaroid film. Construction of such instruments makes a good student project, especially if it leads into a study of the underlying molecular structures. See references *3R-6-8* for additional information.

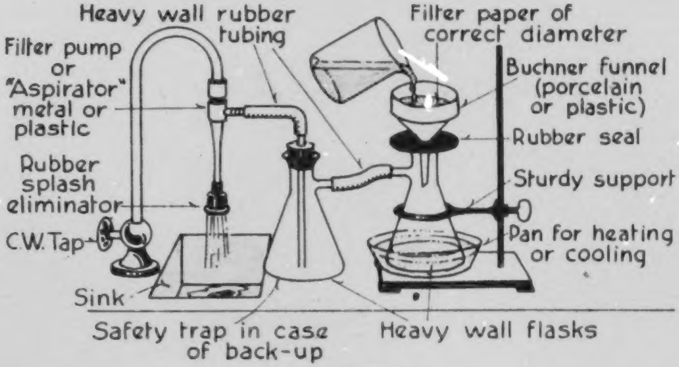
3.35. Degrees of Saturation—Saturated and Unsaturated

Weigh out 50-gm. portions of photographer's hypo crystals (sodium thiosulfate, $Na_2S_2O_3.5H_2O$). Add 50 gm. of the hypo to 200 ml. of water in a beaker and stir until all the crystals have dissolved. Dissolve another 50 gm. of hypo crystals in the same solution which can now be called concentrated. Continue to dissolve 50-gm. portions in like manner until some crystals remain undissolved despite stirring. Take the temperature of the solution and calculate the approximate solubility of hypo at this temperature (the solubility of the hydrate rises from 79.4 gm. per 100 ml. at 0°C. to 291.1 gm. at 45°C.). Discuss the dynamic equilibrium between the crystals and solution.

Filter some of the solution to separate the crystal phase from the solution phase. To show that the solution is still saturated, return some of the crystals previously removed by filtration. They do not dissolve because equilibrium between the two phases was not disrupted by filtration. Equilibrium continues to exist after filtration because the crystal phase required for equilibrium consists of infinitesimal crystalloids that passed through the pores of the filter paper.

3.36. Supersaturated Conditions—Hypo

Continue to add more hypo to some of the solution from activity 3.35 until the solution is saturated at approximately 75°C. Raise the temperature a degree or two more to insure complete solution. If the solution is cloudy, raise the temperature 10 degrees more and filter while hot with the aid of suction (see diagram 3.36). If necessary,


Heavy wall rubber tubing
Filter pump or "Aspirator" metal or plastic
Rubber splash eliminator
C.W. Tap
Sink
Safety trap in case of back-up
Filter paper of correct diameter
Buchner funnel (porcelain or plastic)
Rubber seal
Sturdy support
Pan for heating or cooling
Heavy wall flasks

3.36

repeat the filtration using the same filter paper, until clear. Protect the solution from dust by covering with cotton or aluminum foil. Cool the solution in ice water or, preferably, allow it to stand until the next day. The clear, supersaturated solution will keep indefinitely.

The precise reasons underlying supersaturation phenomena are not entirely clear, but the condition is always upset if a small crystal of hypo is added. Apparently the "seed" acts as a nucleus or center of deposition about which the excess solute separates out in the form of crystals. Add a single crystal to part of the supersaturated solution of hypo. It will produce one large site of crystallization. If a powdered crystal were used it would produce many centers of crystallization simultaneously. Feel the flask to detect the heat of solution being released. Ask pupils when this heat entered into the solution in the first place. Try seeding another supersaturated solution of hypo (monoclinic crystal system) by means of a crystal of sodium chloride. Crystallization will not take place because common salt belongs to a different crystal system (cubic).

Since hypo crystals "melt" at 45-50°C., due to their own water of crystallization, a supersaturated solution can be prepared rapidly. Carefully melt the crystals in a dry flask, without adding any water; then cool. The flask should be protected from dust with a wad of cotton, revolved continuously during the heating to avoid decomposition of the salt and removed from the source of heat as soon as solution has been effected.

3.37. Other Supersaturated Solutions

Supersaturated solutions may also be demonstrated by using sodium acetate or sodium sulfate. Prepare and seed these supersaturated solutions using the method described for hypo. Try melting sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$) in the dry state.

Many organic combinations form similar supersaturated states. Warm 15 gm. of methyl oxalate in 100 ml. of methyl alcohol and cool. Induce crystallization by seeding or agitation and note at the same time the latent heat of solution.

These demonstrations can be made visible to the class to a spectacular degree by performing them in a petri dish on the overhead projector (see appendix *B-1*). Try 66 gm. of hypo plus 15 ml. of water or 35 gm. of hydrated sodium acetate in 20 ml. of water.

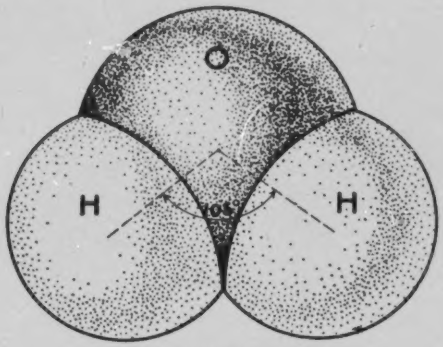
3.38. Mixed Solutes—Common Ion Effect

Prepare a saturated solution of sodium chloride by adding an excess of salt to water. Allow it to stand overnight; then filter. Show that a solution that is saturated for one solute can dissolve portions of another solute by adding a crystal of potassium permanganate to a portion of the above solution. Shake the mixture if necessary until the characteristic color of the permanganate ion results. This effect is limited.

To another portion of the saturated sodium chloride solution in a tall cylinder add hydrogen chloride gas (first dried by passage through a calcium chloride tube if necessary). A precipitate of sodium chloride will form due to the increase in the chloride ion concentration as the hydrogen chloride dissolves. The general term "salting out" is applied to the process of separating a solute from a solution by adding a competing solute.

3.39. Solvents—Water

Exhibit a three-dimensional model of a water molecule showing the 105° bond angle (see diagram 3.39). Such models can be constructed readily from rubber balls or large styrofoam spheres of the type used for Christmas decorations (see appendix *B-2*). With the aid of this model show how the evident properties of water arise.



3.39

An excellent display may be achieved by making four such models. Color one model purple to represent the (unreal) situation of a homogeneous distribution of electrical charges in the molecule. Identify the color blue with negative and the color red with positive charges. Therefore, in this case a blend of the two colors, or purple, is used.

Color two of the models so that the oxygen atom is a reddish blue (indicating that electrons favor the oxygen region of the molecule) and both the hydrogen atoms are a bluish red (indicating that they tend to possess their share of electrons less perfectly). The combination of shape and color in these models indicates clearly the dipolar nature of the molecule. Use the same two models to indicate how a weak bond forms between the negative oxygen of one molecule and the positive hydrogen of an adjacent molecule. This presents an opportunity to point out that the true formula for water is $(HOH)_x$, where x represents the average length of "chain" due to hydrogen bonding. This "chain" becomes larger as the water is cooled and smaller as it is heated, reaching a value of one in steam. This structure underlies the abnormally high boiling point of water. Contrast with other small molecules that do not have hydrogen bonding, such as H_2, O_2 and CO_2.

Pupils can design and carry out an experiment to show that water becomes less viscous as the temperature is raised. The experiment involves an investigation of the variation in speed of filtration with temperature.

The fourth model is colored so that one hydrogen is a true red color and separable from the rest of the molecule to represent a hydrogen ion. The other hydrogen remains attached to the oxygen and both are a true blue color to represent the hydroxide ion. Use this molecule to represent the small but important fraction of water molecules that are always dissociated in the ionic state. Show with the models that the free hydrogen ion would be strongly attracted to the hydroxide ion if it could find one in water. However, as long as it is virtually surrounded by an ocean of covalent water molecules, it exists as a hydronium ion. These models will find innumerable occasions for use during the course. Their initial construction can often be handled best by a student. In the absence of models colored chalk diagrams will be of some help (see references *3R-9*).

3.40. Solvents—Other than Water

a. Drop a crystal of naphthalene into water, another into chloroform.

b. Add kerosene or mineral oil to test tubes containing (1) water and (2) carbon tetrachloride.

c. Add some benzene to (1) water, (2) acetone.

d. Mix a little butter and brown sugar and divide into two portions. Stir one portion with hot water. Stir the other with ether at room temperature. *CAUTION: Use the hood and avoid an open flame when using ether.*

3.41. Tinctures

Divide a quantity of chopped colored flowers, fruits or vegetables between two beakers. Add water to one, ethyl alcohol to the other and stir. After allowing them to stand for a while, filter and compare the two liquids for solvent ability. Solutions in which ethyl alcohol is the solvent are called tinctures. They find extensive use in pharmacy.

3.42. Solvent Extractions

Illustrate the research and industrial technique of separating a component from a solution by coaxing it into a solvent in which it is still more soluble. One ml. of methyl red solution (made by adding 0.02 gm. of methyl red to 50 ml. of alcohol, then adding 50 ml. of water) is added to 50 ml. of water in a separatory funnel. Ten ml. of ether (*CAUTION: Have no flames around*) is added, and the dye is extracted from the water (see diagram 3.23). Extract a second time with a fresh 10-ml. portion of ether and combine with the first ether layer in a beaker. Repeat as often as necessary until all the dye has been extracted from the water, leaving it perfectly clear. Point out that extraction by small portions like this is more efficient, due to the establishment of an equilibrium between the quantity of dye dissolved in the water and the quantity dissolved in the ether. A doubting pupil can find that this is so by attempting to get the dye out all at once with one 50-ml. portion of ether.

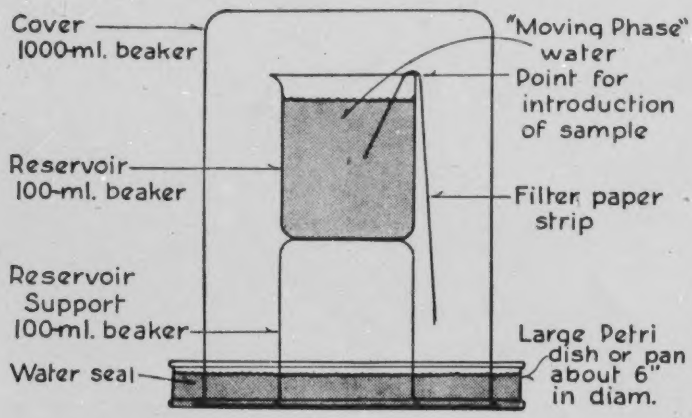
A similar demonstration can be worked out for the extraction of iodine from water with carbon tetrachloride. These demonstrations illustrate the basis of the technique used to separate zirconium from hafnium and uranium from vanadium. Fission products, such as plutonium, as well as many substances in the petrochemical and organic fields are separated in this manner.

3.43. Chromatography

This technique is of critical importance to modern chemistry. Some areas of research have been able to progress only because of their unique ability to perform delicate separations of closely related molecules in solutions, such as the separation of amino acids in protein digests. In principle the method is closely related to the separation of mixtures by liquid solvent extraction discussed above. An additional feature in effect repeats the process automatically many times over, gradually producing a separation of molecules so similar that all other techniques fail to separate them.

In chromatography, a small amount of the mixture to be separated is sorbed on a "fixed phase" consisting of a column or strip of a chemically inert substance with high surface-to-volume ratio. Alumina, nylon powder and paper are examples of "fixed phases." A "moving phase" consisting of a liquid in which the components of the mixture have small but definite solubilities is passed over the "fixed phase," flowing past the sorbed mixture. Because of differences in solubilities in the "moving phase" and differences in degree of sorption by the "fixed phase," the components pass down the column or strip in the same direction as the "moving phase," with velocities depending directly on solubility and inversely on sorption. Thus, in general, the components will move at different velocities to each other and will be separated one from another by virtue of this fact. There is no way to predict the best choice of phases for a particular separation; they must be worked out by trial and error. Both teacher demonstrations and pupil laboratory assignments may be used to illustrate the technique.

a. Cut strips of filter paper, 5 to 6 inches long by $\frac{3}{8}$ to $\frac{5}{8}$ inch wide. Fold them sharply about $1\frac{1}{4}$ to $1\frac{1}{2}$ inches from one end. Assemble the apparatus as shown in diagram 3.43*a*, temporarily omitting the filter paper and the 1,000-ml. beaker.


Cover
1000-ml. beaker
"Moving Phase"
water
Point for
introduction
of sample
Reservoir
100-ml. beaker
Filter paper
strip
Reservoir
Support
100-ml. beaker
Large Petri
dish or pan
about 6"
in diam.
Water seal

3.43a

Note: Whatman's *No. 1* grade, $12\frac{1}{2}$ cm. or larger in diameter, is suitable for this experiment both as to rate and sorbing tendency. Quantitative grades, such as Whatman's *No. 50* are slower, although they may give better separations. Similar grades of other manufacturers will serve also. The very free-flowing grades (designated "for qualitative work" or "rapid") or very thick, soft papers should be avoided, as separation is likely to be unsatisfactory. With a thin glass rod made by drawing out the end of a stirring rod, place a small drop of ink on the center line of the long end of the filter paper strip about ¼ inch away from the fold. An inkspot about 1/16 inch in diameter gives the best results. After it has dried you may add more ink to the same spot to build up the concentration without increasing the diameter. When dry, hang the strip in the apparatus as shown in the diagram, taking care that the short end is immersed in the water in the reservoir (to act as a wick) and the long end is not immersed in the water of the seal. Place a 1,000-ml. beaker over the assembly to prevent evaporation from the paper.

Water will be wicked along the filter paper at a rate of about 0.[illegible] cm. per minute when using the paper and conditions suggested. As the water passes the inkspot, separation of the black spot into colored streaks begins. After about 20 or 30 minutes from first contact between water and spot, there should be several colored streaks at various locations on the strip. Shaeffer's Skrip, *No. 32* jet black permanent gives yellow, red and blue streaks. Other fountain pen inks will be found to function well, but not drawing, spotting or "India" inks. Try artists' water colors also. An interesting demonstration of differences among inks can be made by sorbing a spot of each of two or more inks side by side on the same strip of paper, developing the chromatograms simultaneously under identical conditions by this expedient. A comparison of "skrip" permanent jet black with "skrip" permanent blue-black or with "superchrome" permanent jet black, for example, is interesting. Handwriting experts use a similar technique to identify the ink used in signatures.

Stop the chromatogram before it reaches the end. Remove the paper from the apparatus and mark the position of farthest advance of the water. Estimate the most dense part of each streak. Measure the distance traveled by the water and by each streak (to the nearest 1/10 inch) from the point of initial sorption of the sample. Substitute the values in the following equation:

$$R_f = \frac{\textbf{distance traveled by dye}}{\textbf{distance traveled by water}}$$

The value of R_f for a properly chosen set of fixed conditions is a characteristic of a particular substance. R_f can be used as an aid in identifying a substance in a complex mixture by comparison with R_f's of known substances treated under the identical set of conditions.

b. Water alone is rarely a good "mobile phase" for chromatography. A variety of aqueous solutions and mixtures of organic solvents are used. Furthermore the substances themselves are generally not colored, but are converted to colored derivatives by chemical reactions after separation.

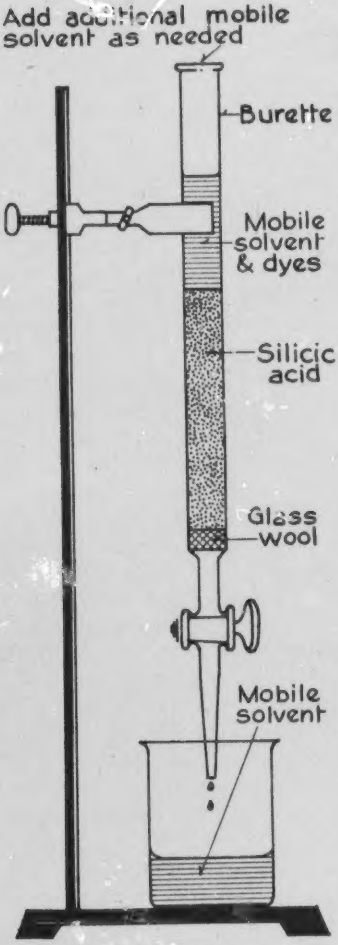
Prepare a solvent by mixing 87 ml. of acetone, 4 ml. of concentrated HCl and 9 ml. of water. Place enough of the solvent in each of two 1-quart mason jars with lids to bring the liquid level about ⅜ inch above the bottom of the jar. Prepare two filter paper rectangles, 6 inches wide by 9 inches long, of Whatman *No. 1* filter paper or equivalent. On the long side of each rectangle draw a fine pencil line about ¾ inch from the edge. At labeled points spaced 1 inch apart along this line place 0.01 ml. of a salt solution of copper (Cu^{++}), iron (Fe^{+++}), Nickel (Ni^{++}), Cobalt (Co^{++}), Silver (Ag^{+}) and Lead (Pb^{++}) respectively. Each solution should have a concentration of 5 milligrams of ion per milliliter. Place on the same line 0.01 ml. of a solution made by dissolving a piece of a copper alloy (size of a penny) in concentrated nitric acid and diluted to a final volume of 100 ml., and 0.01 ml. of a solution of a silver alloy made from a piece the size of a nickel or a dime in the same way (other metals may be substituted).

Spot each piece of filter paper with the eight solutions. Keep the spots as small as possible. Wait for them to dry thoroughly. Bend the paper around to form a cylinder 6 inches high and sew the edges together, with no overlap, so there will be no double thickness of paper to cause irregular flow. Place the paper cylinders in the mason jars so that the row of dots of metallic ions is just above the level of the liquid. Put the covers on the jars and allow to stand about 30 minutes, until the solvent almost reaches the top of the paper. Remove the cylinders, mark the solvent front, and allow them to dry completely. Expose one of the papers to hydrogen sulfide gas in a hood. Then spray the other paper (spread out flat) with a 5 percent solution of ammonium sulfide in an atomizer, or paint lightly with a cotton-tipped stick dipped into the solution. From the color and R_f of the spots, determine the ions present in the alloys.

c. Columns of powdered solids were used in chromatography before the use of paper became so popular, and the method is still used where larger quantities must be separated.

Try the separation on a silicic acid column of the two dyes *D* and *C* Violet *No. 2* and *D* and *C* Red *No. 18*. The mobile solvent is a saturated solution of nitromethane in normal hexane. In 50 ml. of the mobile solvent, dissolve 25 mg. of each dye. The solution containing the dyes is added to the column and the dyes are "chased" through the column by the addition of more of the mobile solvent (see diagram 3.43*c*).

Another example is the separation of the various color components from a petroleum ether extraction of green leaves, using powdered sugar as the adsorbent. The sugar column is mixed with a 9:1 petroleum ether and benzene mixture. Anthracene, phenanthrene and


Add additional mobile solvent as needed
Burette
Mobile solvent & dyes
Silicic acid
Glass wool
Mobile solvent

3.43c

naphthalene may be separated on activated alumina, using ultraviolet light to follow the bands, and 95 percent ethyl alcohol as solvent. In this case attractive colored fluorescences are shown.

d. Chromatography can be used for separations in radioactivity studies. The mixture is spotted on filter paper, separated with a suitable solvent, dried, and the R_f determined with the aid of a Geiger counter, which will also measure the quantity of each component present.

3.44. Gas Chromatography

A highly successful technique for the separation of gaseous mixtures and substances that can be vaporized readily with heat has been developed recently. Its use has spread rapidly throughout research and industrial laboratories, and its role in the progress of modern chemistry should not be ignored. It resembles ordinary chromatography in that it employs a similar column of a solid, often in combination with an adsorbed liquid. The moving solvent is a gas, frequently helium, and the tiny sample is vaporized into the gas stream. The column is generally heated, and the exiting gas flows past an electronic detector far more sensitive than possible in the techniques of ordinary chromatography.

One simple form of detector is a thermistor, a resistor whose value fluctuates with temperature. The rate of transfer of heat by a gas is inversely related to its molecular weight. Thus the separated gaseous components of the original mixture can be detected as they exit by the changes in current flow (due to Ohm's Law) in the detecting circuit. The separate fractions can be recovered by freezing if desired. The detection principle can be demonstrated quite easily with a small resistance heater of the conical shape made to fit into an ordinary light socket. Adjust the current with a rheostat or light bulb in series, so that the resistance wire glows a dull red in air. First, immerse the glowing resistance in a beaker of carbon dioxide. Since the heavier molecules travel more slowly than air, they carry the heat away more slowly, and consequently the wire glows a brighter red. Next, invert a beaker of helium over the glowing wire, and it loses brightness due to the more efficient cooling.

While commercial instruments are expensive, construction of a basic instrument for gas chromatography is within the powers of keen students. Consult a recent text on "instrumentation" or "instrumental methods of analysis."

3.45. Suspensions

Dissolve a teaspoon of $NaCl$ in 500 ml. of water in a glass cylinder. Add a teaspoon of clay or mud to an equal amount of water in another cylinder and shake each. Attempt to separate each by filtration.

To show the difference between suspensions and colloids, add two drops of HCl to a test tube containing 25 ml. of a 1 percent freshly prepared gelatin solution and two drops of HCl to another containing 25 ml. of water. Add a few drops of silver nitrate solution to each test tube. Colloidal $AgCl$ forms in the first test tube and a suspension forms in the second. Allow the tubes to stand and observe the rate of settling.

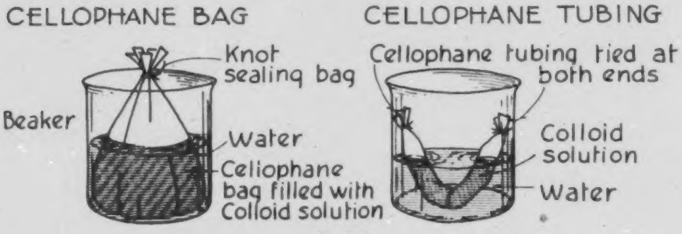
3.46. Colloids

Illustrate the intermediate position of colloids with respect to solutions and suspensions. Place three large beakers on a table. The center beaker should contain hot, distilled water, and the other two should contain tapwater at room temperature. With a medicine dropper or pipette add a 37 percent ferric chloride solution to the first beaker and stir until it has a moderate yellow color. Note the number of drops used (30-50) to prepare this true solution. To the hot water in the second beaker, add and stir one or two drops of the $FeCl_3$ solution. Compare the color in the two beakers. Continue adding drops until as many as 40 drops have been added. The deep red color is due to hydrolysis of the salt. Accelerated by the higher temperature, a clear colloidal solution or sol of "ferric hydroxide" is produced and stabilized by positive charges. To the third beaker add a few ml. of any base, then some of the $FeCl_3$ to produce a coarse suspension of noncolloidal ferric hydroxide which soon precipitates.

3.47. Particle Size of Colloids—Surface Area

a. In general, true solutions contain molecules, atoms or ions less than 1 millimicron (1×10^{-6} mm.) in diameter. In contrast, the colloid range is 1 to 100 millimicrons and particles in coarse suspensions are larger than 100 millimicrons. This division is arbitrary, and the boundaries are *not* sharp.

The difference in particle size may be illustrated by subjecting portions of the contents of the three beakers from activity 3.46 to the process of dialysis. This process is illustrated in diagram 3.47. Allow the dialysis to proceed for several minutes and then test the water in the beakers with potassium ferrocyanide solution as indicated before. Only the true solution contains particles small enough to pass through the membrane. The dialyzate from the third beaker will give a positive test for a base with phenolphthalein.



3.47

A model of the dialysis mechanism is made with a glass jar, small yellow beads and larger red marbles. The cap of the jar should contain several holes a little larger than the beads but too small for the marbles to pass through. Shake the beads through the cap of the jar to illustrate why the "ions" from the first beaker can come through the membrane while the "colloidal particles" in the second cannot. Dialysis, an important technique in biochemistry, is the process used by doctors in the "artificial kidney."

b. Colloidal particles are much heavier than particles in true solutions.

(1) Fill each of two test tubes three-fourths full with a clear gelatin solution. Mix one part of gelatin to six parts of hot water and allow to gel. Add a quantity of copper sulfate solution to one test tube and an equal amount of ferric hydroxide sol to the other. Allow to stand overnight. The relative sizes of the two particles are shown by the rate at which they diffuse through the gel.

(2) Add a few drops of potassium ferrocyanide solution to a gelatin solution and several drops of phenolphthalein solution to turn it pink. Fill a large test tube two-thirds full with this mixture and allow it to gel. Now fill the remainder of the tube with dilute $FeCl_3$ solution. Hydrogen ions diffuse readily through the gelatin and turn the phenolphthalein white. The larger ferric ions diffuse more slowly and form Prussian blue with the potassium ferrocyanide. After several days, three bands of color will be seen in the tube: blue at the top, white in the middle and pink at the bottom.

c. Most of the special properties of colloids are due to their great surface.

Prepare lead tartrate by mixing a hot solution containing 70 gm. of rochelle salt in 100 ml. of water with one containing 60 gm. of $Pb(NO_3)_2$ in 100 ml. of water. Cool, filter, and dry the solid by pressing it between filter paper. Gently heat about 10 gm. of lead tartrate in a test tube until thoroughly charred and stopper immediately. It will keep indefinitely, but will ignite spontaneously when shaken into the air.

3.48. Centrifuges

Many precipitates form fine suspensions that are difficult to filter because they clog the pores of the paper or pass through. By multiplying the apparent weight of the particles, the centrifuge deposits them more rapidly than by unaided gravity. The clear filtrate can then be decanted. The ultra-centrifuge can precipitate proteins from solution without altering them chemically and is therefore a most useful tool for the biochemist. If the class has not already used centrifuges, exhibit one and demonstrate its correct use. Be sure to emphasize the importance of balancing the tubes in the centrifuge in order to avoid vibration.

3.49. Importance of Colloids—Types

Have the pupils list 10 materials they have contacted since arriving at school. The following are examples of some materials whose properties are totally or partially due to colloidal effects: textiles, dyes, paints, paper, inks, photographs, soil, rubber, foods, fog, clouds and cosmetics. Blood, lymph, milk, sap, viruses, plant and animal protoplasms are examples of colloidal solutions.

Types of colloids: (Gases form true solutions with other gases, leaving eight possible categories.)

- *Gas in liquid*—foams; such as aerosol shaving cream and foamite fire extinguishers
- *Gas in solid*—foam rubber, floating soaps containing air
- *Liquid in gas*—fogs; clouds, "steam" rising from a beaker of boiling water
- *Liquid in liquid*—emulsions; milk and mayonnaise
- *Liquid in solid*—gels; gelatine desserts and jellies
- *Solid in gas*—smokes; ammonium chloride smoke and cigarette smoke
- *Solid in liquid*—sols; paints, inks and toothpaste
- *Solid in solid*—certain alloys, minerals and colored glasses

3.50. Preparation of Colloids

a. Smokes. Burn a little red phosphorus to form a smoke of phosphorus pentoxide, P_4O_{10}. Expose some titanium tetrachloride to air. It will react with water vapor in the air to form HCl and a smoke of titanium dioxide which is used in "sky writing."

b. Gels. Mix 20 ml. of a saturated solution of calcium acetate with 180 ml. of 95 percent ethyl alcohol. Squeeze out the liquid, dry hands place gel on asbestos and ignite. This is similar to "canned heat."

To 10 ml. of sodium silicate solution (water glass) add 30 ml. of concentrated HCl. This silica gel can be washed free of acid, oven dried and used as a desiccant.

c. Sols.

(1) See activity 3.46 for the preparation of ferric hydroxide sol.

(2) See activity 3.53*b* for the preparation of a sulfur sol; or, add

a pinch of sulfur to 1 ml. of ethyl alcohol in a test tube. Heat for one or two minutes in a waterbath, being careful not to boil the alcohol. When most of the sulfur has dissolved, pour the clear solution into a 2-ounce widemouthed bottle three-fourths full of water. The sulfur is displaced from the alcohol solution when diluted with a large volume of water.

(3) Add 1 gm. of arsenious oxide, As_2O_3, to 100 ml. of distilled water. Boil, cool and filter. Add a solution of sodium sulfide or bubble hydrogen sulfide through to form the As_2S_3 sol which runs through filter paper. Save the sol for examination over a period of weeks.

(4) Prepare a gold sol by making a 1 percent solution of gold chloride (available from photographic suppliers) in distilled water. Add this slowly, a drop at a time, to a solution containing 10 ml. of stannous chloride in 150 ml. of distilled water. Note the colors as they vary with the size of the gold articles. Better colors are obtained if 1 ml. of the 1 percent gold chloride solution is added dropwise to 200 ml. of distilled water containing a little potassium carbonate and formaldehyde (40 percent solution in water). Boiling may hasten the action.

(5) Prepare a starch sol by grinding some starch vigorously in a mortar with a pestle. Add water to the starch and stir. Filter this mixture and test the filtrate with iodine solution. The simulated action is that of a colloid mill.

3.51. Precipitation of Colloids

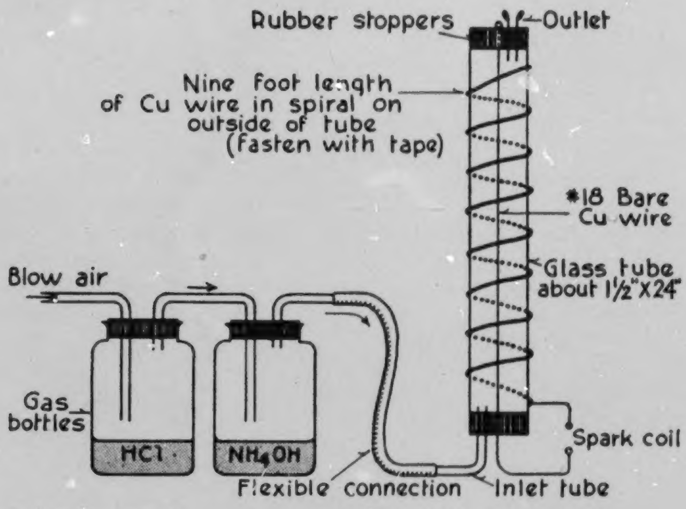
Metallic hydroxides and sulfides generally form sols whose particles have a positive surface charge, while negative types are formed by sulfur, arsenious sulfide, silicic acid, graphite and the noble metals.

a. **Mutual Precipitation.** Combine equal portions of $Fe(OH)_3$ sol (positive) and As_2S_3 sol (negative). The original charges arose due to selective absorption of ions from the solution.

b. **Precipitation by Ions.** Add a few drops of glacial acetic acid to India ink to precipitate the colloidal carbon, or to fresh milk to precipitate casein. To 10-ml. portions of a negative sol such as As_2S_3, add 1 ml. of 1M solutions of Na^+, Ca^{++} and Al^{+++}, and compare their effectiveness as precipitants. This illustrates both the action of commercial flocculating agents in speeding up the precipitation of substances before filtration and the formation of river deltas as colloidal clay particles meet sea water.

c. **Precipitation by Electricity.** Introduce two electrodes from an 8-volt direct current source into a beaker containing an arsenic sulfide sol. Pass the current through the colloid for about 10 minutes. The arsenic sulfide will be coagulated on the positive terminal. Rubber can be deposited from latex in a similar fashion.

Demonstrate the Cottrell precipitator. See diagram 3.51. Instead of the ammonium chloride smoke, a lighted cigarette may be placed in the upper outlet and a suction hose attached to the inlet at bottom. The apparatus should be dry. Reversing polarity may improve the performance.


Rubber stoppers
Outlet
Nine foot length of Cu wire in spiral on outside of tube (fasten with tape)
#18 Bare Cu wire
Glass tube about 1½"X24"
Blow air
Gas bottles
HCl
NH$_4$OH
Spark coil
Flexible connection
Inlet tube

3.51

3.52. Protective Colloids

Colloids can receive additional stability from the presence of a third component which established itself at the boundary between the dispersed and continuous phases. Such stabilizers may function in several ways such as: by increasing the electrostatic charge, by protecting the colloidal particle from neutralization of its charge, or by a detergent effect due to molecules that dissolve partly in the dispersed phase and partly in the continuous phase.

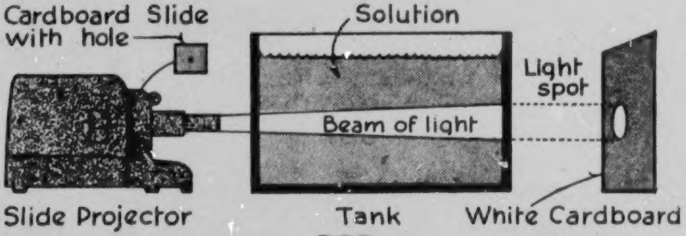
Prepare some simple "baking powder" by mixing sodium bicarbonate powder and powdered aluminum sulfate. Add water and note how long the foam lasts. Add powdered aluminum, or white of egg before the addition of water, and compare the results. Local fire departments are often willing to demonstrate the effectiveness of "foamite" extinguishers.

3.53. Tyndall Effect

a. In a darkened room direct a narrow intense beam of light through beakers containing solutions of copper sulfate, sodium chloride, ferric hydroxide sol, arsenic sulfide sol and pure water. Glassware should be carefully cleaned and all solutions filtered through a dense paper before they are used.

The ultramicroscope (standard microscope with special lighting device) operates on the Tyndall effect. It can be assembled as a student project (see reference *3R-10*).

b. A variation of the Tyndall effect is known as the "synthetic sunset" demonstration. See diagram 3.53. The solution in the aquarium or battery jar contains 10 gm. of sodium thiosulfate per liter of solution. To this add 5 ml. of concentrated hydrochloric acid for every liter of solution and stir. Darken the room. As colloidal sulfur slowly begins to form, the projected light turns red, then extinguishes. From the side the scattered light appears blue because short wavelengths are more easily scattered. This duplicates a sunset observed through the dust layer close to the earth. For polarization effects, see the *Physics Handbook*, activity 3.30. Instead of using colloidal sulfur to produce this effect, try adding milk to water a few drops at a time.

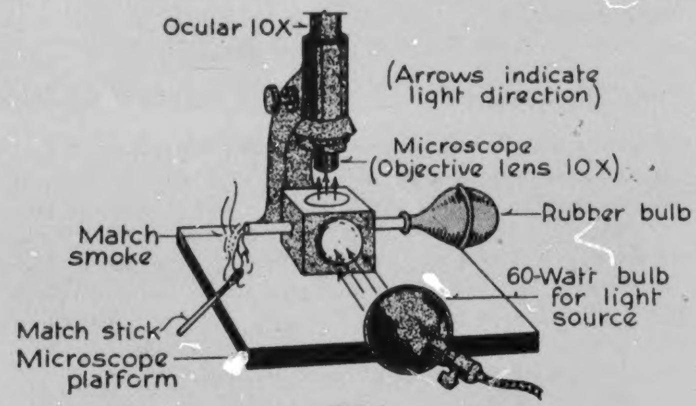


3.53

3.54. Brownian Motion

A microscope may be used to observe the Brownian movement as shown in diagram 3.54. For best results use only a little smoke and replenish the supply every few minutes. If a totally dark room and a good arc light are available, projection of the motion may be successful if the projector is kept near a good beaded screen. Try using carmine dye powder in pure methanol placed on a concave microscope slide.

Simulated Brownian motion can be observed by scattering powdered camphor crystals on water in a petri dish placed on the overhead projector (see appendix *B-1*).



Ocular 10X
(Arrows indicate light direction)
Microscope (Objective lens 10X)
Rubber bulb
Match smoke
60-Watt bulb for light source
Match stick
Microscope platform

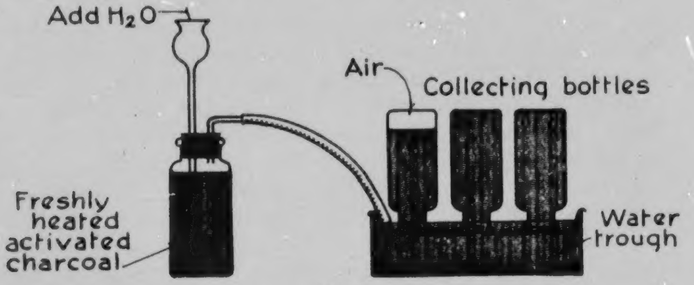
3.54

3.55. Adsorption by Colloids

a. Fill a 200-ml. bottle with freshly activated charcoal (activated by heating and cooling in a covered crucible). Arrange apparatus as shown in diagram 3.55. Add water to the bottle slowly and collect the displaced air over water. Compare the volume of air collected with that of the bottle containing the charcoal.

b. Add some hydrogen sulfide water to a test tube and note the odor. Place some activated charcoal in the tube, stopper it securely and shake it from time to time. Compare with the original odor after 15 minutes.

c. Prepare colored solutions of any of the following: brown sugar, molasses or licorice, indigo and methylene blue, or malachite green solution. Add a spoonful of activated charcoal to the liquid in a beaker. Stir, heat gently and then filter. As a control, try the same procedure using a copper sulfate solution.



Add H_2O
Air
Collecting bottles
Freshly heated activated charcoal
Water trough

3.55

d. Boil some cider vinegar with activated charcoal and filter. Test the filtrate with litmus. Note both odor and taste.

3.56. Emulsions

Demonstrate the formation, types and stability of emulsions.

a. Add equal amounts of kerosene and water to a glass cylinder. A little copper sulfate solution may be added to help identify the water layer. Allow it to stand for a short time. Add 1 ml. of soap solution and shake again. This is an oil in water *(O/W)* type emulsion.

b. Place 100 ml. of level oil in an electric blender and start blender Then add 7 ml. *Span 85,* 6.6 ml. *Tween 81,* and slowly, 100 ml. of distilled water. (*Tween* and *Span* are commercially available emulsifying agents; see reference *3R-11.*) This is *(W/O) type.*

c. Mix 5 ml. of oleic acid and 30 ml. of kerosene; then stir thoroughly while adding 20 ml. of 10 percent triethanolamine in water. Test this emulsion, a "waterless" hand cleaner, by trying to remove some oil or grease from the hands.

3.57. Amorphous Substances

Set up three flasks containing air, water and sugar. Call attention to the freedom of the molecular motion in each. Review the demonstration of Brownian motion (see activity 3.54).

Give examples of amorphous solids. Exhibit samples of flowers of sulfur, carbon black and finely powdered aluminum. Point out that the majority of such powdered solids are amorphous only to the human eye. With some care a small list of solids can be drawn up which show a very low degree of order, or only regions somewhat crystalline in a matrix of random arrangement; for example, glasses (technically a supercooled liquid), and random-coil proteins. Even rubber has crystalline regions (see reference *3R-12*).

To show that it is dangerous to consider a solid as amorphous, demonstrate how easy it is for crystals to form. An analogy to crystallization may be demonstrated by "crystallizing" some marbles. Shake a number of marbles (or preferably ball bearings) in a plastic box. The marbles represent molecules. While in violent motion they represent the gas phase. When they are permitted to "cool" and "crystallize" in a corner of the box, they are found to have close-packed themselves in regular rows and layers, with the familiar pyramid arrangement of cannon balls. Point out that the crystalline tendency in nature (ordered arrangement), far from being mysteriously achieved is the simplest to fall into, especially with the aid of intermolecular attractions. This demonstration can be projected to great advantage by placing some shell shot in a covered petri dish for use with the overhead projector. Shake the dish to represent the disorder of a gas. Then stop the agitation, tipping the dish slightly and the spheres will collect in regular arrays (see reference *3R-13*). To reduce this demonstration to the real situation exhibit a few iodine crystals in a flask. Next, warm them over a bunsen burner to produce the visible violet vapor, and finally cool the flask under the tap to reform the crystals. This demonstration also projects well if a culture flask with flat sides is used. Have pupils indicate the relationship between the shell shot in the petri dish and the iodine in the flask.

3.58. The Geometric Form of Crystals

a. Exhibit a large and well-formed crystal of copper sulfate or rochelle salt. To emphasize the regular geometry show a larger plastic model of the crystal made by cementing together sheets of clear or colored plexiglas (or solid plexiglas; see reference *3R-14*). Finally relate these models to an exhibit of the internal crystal structure made with a ball and peg crystal model set.

b. Show a variety of crystals from materials found in the chemistry stockroom, such as:

CRYSTAL FORM	EXAMPLES
Cubic	NaCl, KCl, KBr, $Ba(NO_3)_2$
Tetragonal	Hg_2Cl_2, $NiSO_4$, SnO_2
Hexagonal	$LiKSO_4$
Rhombic	KNO_3, I_2, $MgSO_4$, $ZnSO_4$, K_2SO_4, $AgNO_3$, K_2CrO_4
Monoclinic	Na_2CO_3, $KClO_3$, $NaC_2H_3O_2$, $BaCl_2$, ($H_2C_2O_4$) Oxalic acid, Na_2SO_4
Triclinic	$CuSO_4$, $K_2Cr_2O_7$, H_3BO_3, CaS_2O_3

Additional information on the crystal form of compounds can be found in a handbook of chemistry or reference *3R-15*.

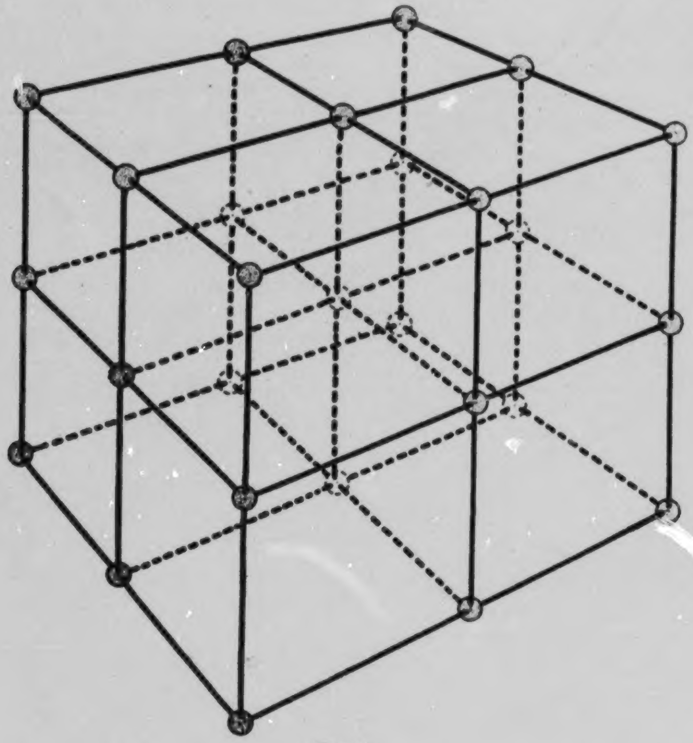
c. Exhibit crystals composed of:

(1) Molecules—such as ice, iodine, naphthalene and benzoic acid. Note the low melting points, and relate this to the attractive forces between the molecules.

(2) Ions— such as potassium bromide, magnesium chloride and barium sulfate. Note the higher melting points and relate to the force of attraction between the ions. Such crystals are often considered to be macromolecules.

(3) Atoms—both nonmetallic elements, such as graphite, sulfur and the red allotropic form of selenium, and metallic elements, such as rods of iron, aluminum and zinc. With the aid of melting points from a handbook discuss their bond strengths.

While not generally apparent all metals are crystalline. This can be seen in the zinc crystals on galvanized pails, on certain brass door knobs and in electro-depositions such as a lead or silver tree. Furthermore, the metallic bond is very strong, which is the basis for the structural use of metals. A pupil may wish to report on current research into perfect metal crystals ("whiskers") and their extraordinary strength. See reference *3R-16*. Reference *3R-17* is a good nonmathematical explanation of crystal forms. Simple valence theory is incapable of explaining this bond. The problem has given rise to several theories,



3.58

but a commonly accepted model can be constructed with a ball and peg set, see diagram 3.58, where the balls represent a lattice of metallic *ions* (the pegs do not represent anything) and the electrons are imagined as a mobile cloud permeating the crystal and not attached to specific ions. It can be seen that an applied e.m.f. would cause the cloud of electrons to drift through the lattice in one direction, thus explaining the conductivity of metals. If the model is assembled with pieces of spring rather than rigid rods, it can be deformed to show the crystal stresses that modify metallic properties in the processes of rolling, drawing and forging.

3.59. Some Properties of Crystals

Some interesting areas for reports and discussions are:

(1) **Allotropic forms**—Display carbon, sulfur and selenium.

(2) **Polarizing crystals**—Under the microscope study calcite, sodium chlorate, potassium hyposulfate and quartz.

(3) **Monolayers**—See Langmuir's simple demonstrations reported in the May 1931 issue of the *Journal of Chemical Education*.

(4) **Crystal repair**—See activity 3.14.

(5) **Crystal purity**—Devise an experiment to show that small rapidly formed crystals of salts are likely to be more pure than large spectacular ones.

(6) **Deceptive forms**—Instead of cubes, octahedrons form when sodium chloride is crystallized from solutions containing urea, ammonium hydroxide or alkalis. This illustrates the dangers that beset a nonexpert who attempts to identify substances by outward appearance.

(7) **Decrepitation**—White crystals of NaCl frequently show a dark center due to mechanically included water. When heated, escaping steam fractures the crystal.

(8) **Partially crystalline solids**—Prepare an exhibit including asbestos, highly crystalline polyethylene, "milk glass" (the white color is due to small centers of crystallization), "Pyroceram" (a fully crystallized glass), animal or human hair (they have a helical protein structure) and other fibers.

(9) **Imperfections in crystals**—See reference *3R-18*.

(10) **Aligned crystals in metals**—See reference *3R-19*.

(11) **Recrystallization**—Crystallize potassium nitrate from a solution containing ferric chloride by evaporating the water from the solution. Dissolve a crystal in a very small quantity of distilled water and test for iron with potassium ferrocyanide reagent. Continue to

dissolve and recrystallize the remaining crystals until pure KNO_3 crystals are obtained.

(12) **Sublimation:** Besides iodine, try heating 5 gm. of hexachloro-ethane in a 1-liter Erlenmeyer flask, or boil 5 gm. of naphthalene in a 1-liter beaker covered with a 1-liter round bottom flask containing cold water.

3.60. Inclusion Complexes

These interesting substances can be used to sharpen the pupils' appreciation of the importance of spacial relations (steric effects) in molecules. They are crystalline mixtures, not true compounds, in which the molecules of one of the components are contained within the crystal lattice framework of the other component. The framework may be in the form of channels, cages or layers. The two components are present in constant but not stoichiometric proportions. The occurrence of the phenomenon is dependent upon appropriate molecular dimensions of both components. Quite diverse substances can be combined, such as argon in hydroquinone or benzene in nickel cyanide ammonia complex. The complexes are stable at ordinary temperatures. Melting or dissolving the crystals allows the entrapped component to escape. They are also called adducts or occlusion complexes.

A subtype is the group called "clathrate compounds." These are inclusion complexes in which molecules of one substance are completely *caged* within the other. This is simple to demonstrate. Saturate 100 ml. of distilled water with hydroquinone at 30°C. Bubble H_2S through the solution until saturated with the gas also. Chili the solution in an ice-salt bath. Small white crystals of the clathrate compound will come down with the H_2S being caged within the hydroquinone. Filter the crystals out and wash while on the filter with ice water. Air dry the crystals. Show the dry crystals and let the students smell them (they are odorless). Dissolve a small amount in distilled water; the odor of H_2S is apparent. Melting the crystals will have the same effect of releasing the H_2S, which will affect wet lead acetate test paper. Recover the hydroquinone and show it to be pure by checking its melting point.

3.61. Crystallizations

Crystallizations can be performed to advantage in petri dishes on the overhead projector. Use thin transparent layers of solution for best effects.

These procedures produce crystals rapidly and are suitable for class demonstrations.

a. Seed a supersaturated solution. See activity 3.36.

b. Dissolve 10 gm. of powdered oxalic acid in 25 to 30 ml. of hot water. Neutralize with ammonium hydroxide and test with litmus paper. Then add a slight excess of NH_4OH. Keep the liquid hot. Filter while hot through a funnel preheated with hot water. Cool. The white crystals are ammonium oxalate.

c. Dissolve flowers of sulfur in carbon disulfide using one gram of sulfur per two milliliters of solvent. Pour onto a watchglass and set in the draft of a window or hood. Within a few minutes rhombic crystals of sulfur will be visible. *CAUTION: Vapor of carbon disulfide in air is explosive; keep from flames.*

d. Spread a little saturated solution of salicylic acid in methanol on a pane of glass and allow evaporation to produce a crystal leaf pattern. Also try benzoic acid in acetone or an aqueous solution of hydroquinone saturated at 80°C.

e. Add a few grains of powdered lead iodide to 50 ml. of boiling water. Stir well and filter this into a graduate that has been preheated by hot water to prevent undue cooling of the solution. As the solution cools, bright spangles of lead iodide will form.

f. Heat a microscope slide until it barely can be handled and then drop melted acetamide or a hot supersaturated solution of salicylic acid on the slide. Spread in a thin layer and allow to cool while being projected by a microprojector.

3.62. Growing Large Crystals

Large crystals can be grown with care and patience. Some good ones to try are: sodium potassium tartrate (rochelle salt), sodium nitrate, citric acid, potassium aluminum sulfate, nickel ammonium sulfate, ferric ammonium sulfate, aluminum sulfate, potassium chromium sulfate (chrome alum), potassium dichromate, magnesium sulfate, sodium chloride, copper sulfate, potassium sulfate, potassium bisulfate and lead nitrate. The following suggestions may be employed by pupils in the laboratory. See also the excellent ideas in reference *3R-20.*

- Clean all apparatus carefully and protect solutions from dust at all times.
- Prepare saturated solutions with distilled water, then filter carefully. Keep temperature constant.
- Rub vaseline around the upper inside rim of the crystallizing dish to arrest creeping.
- Evaporate slowly by supporting a plate of glass over the container so that there is about one-half inch clearance between

them, or cover with a circle of filter paper.

- After a few days small crystals will form. Select the one with most perfect shape and place in another container to act as seed crystal. Cover again with filtered saturated solution. Inspect daily and add more saturated solution when required. Scrape off small bud crystals that form on the large one, and turn the crystal to promote even growth.

Another successful method well worth trying is the following: Place two 75-ml. crystallizing dishes containing solutions with excess crystals (not filtered) 5 cm. apart in a 2-liter jar. Next, carefully cover over with distilled water. A layer of melted paraffin is poured across the water surface to seal the systems. Large crystals form during a two to six week period. Satisfactory pairs of reagents are: sodium thiosulfate and barium nitrate, calcium chloride and sodium hydroxide, lead nitrate and sodium chloride, sodium sulfate and lead nitrate, barium chloride and ammonium oxalate and silver nitrate and sodium nitrate.

3.63. Water of Crystallization—Hydrated Salts

Due to the dipolar nature of water, ions in solution exist in a hydrated condition. In certain cases the water molecules are more tightly bound in coordinate covalent bonds. When ions crystallize, water molecules are sometimes included in the lattice structure in a definite ratio. Such water is regarded as held by true chemical bonds. In some cases (as in efflorescent crystals), the bonds are very weak. In other cases (some minerals), the bonds are stronger and quite stable.

Heat small samples of crystals of the following substances in test tubes: copper sulfate, barium chloride, cobalt nitrate, alum and sodium chloride. Although sodium chloride is not a hydrate, it crystallizes with a small amount of water that is held mechanically. When the crystal is heated, this water is converted to steam thus causing the crystal to break apart forcibly.

3.64. Quantitative Analysis of a Hydrate

This is an excellent exercise for pupil laboratory work if moderately sensitive balances are available. Stress the techniques and mathematics involved.

Prepare a small crucible by cleaning, drying, heating a minute or two to vaporize any remaining impurities, and allow to cool. Handle the crucible with a piece of paper to avoid a deposit from finger marks. Record its weight to the nearest *thousandth* of a gram. Place barium chloride crystals ($BaCl_2 \cdot 2H_2O$) in the crucible until half-filled and weigh again with the same accuracy and record. Heat gently at first, then to maximum red heat for 10 minutes; cool and reweigh. Reheat for 5 minutes, cool and weigh again. Repeat this process until two successive weighings give the same results. An allowance of a few thousandths of a gram can be made depending on the type of balance used. Calculate from the data determined experimentally the percentage of water and the nearest whole number value for x in the formula $BaCl_2 \cdot xH_2O$. Other salts can be used with somewhat less satisfactory results; for example, $CuSO_4 \cdot 5H_2O$ or $FeSO_4 \cdot 7H_2O$. See also, Manufacturing Chemist's Association, *Scientific Experiments in Chemistry*, "Composition of a Mixture."

3.65. Efflorescence

a. Counterpoise some crystals of hydrated sodium sulfate or hydrated sodium carbonate on a beam balance. Note the translucent character of the crystals. Observe the position of the balance at the end of the period and the change in the structure of sodium sulfate. Some hydrates have high vapor pressure and as a consequence lose their water of hydration readily to the air.

b. Pulverize some blue vitriol crystals and heat in an ignition tube until white. The tube should slant downward to permit water to drip out. Spread the anhydrous salt on white paper when cool. Squirt water on it from a wash bottle and observe.

3.66. Deliquescence

a. Counterpoise some calcium chloride or solid sodium hydroxide in a watchglass. At the end of the period, observe the position of the balance and the appearance of the sodium hydroxide.

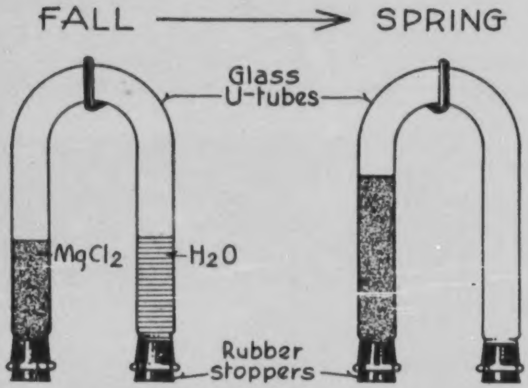
b. Display calcium chloride drying tubes and desiccators. Explain their use in the laboratory.

c. Set up an inverted U-tube as in diagram 3.66. One arm is to be half-filled with water, the other with crystals of magnesium chloride. Hang the device where the class can follow progress of deliquescence during the school year from fall to spring.

d. Add to some ethyl alcohol or gasoline that has been shaken with water, some powdered anhydrous copper sulfate. The blue color is a chemical test for water.

3.67. Efflorescence and Deliquescence

This is a long-term project for a student with the necessary interest, ability and patience. Considerable data are to be collected and inter-



3.66

preted. Graphs can and should be constructed.

Use clean, dry, large test tubes. Place a known amount of anhydrous copper sulfate in a test tube. Push horizontally an equal quantity of $Na_2CO_3 \cdot 10H_2O$ to within an inch of the copper sulfate. Stopper, and keep the tube horizontal. Determine the time required for the copper sulfate to assume a blue color by the efflorescence of the hydrate (about a half hour).

Repeat the exercise by:

- Varying the distance between the two salts
- Using other efflorescent hydrates
- Substituting calcium chloride for anhydrous copper sulfate
- Varying the relative amounts of the two salts
- Varying the temperature
- Varying the humidity (correlate with relative humidity)
- Using reduced pressure in the test tube

3.68. Drying Agents and Their Use

Exhibit samples of the following substances and discuss their uses.

- Concentrated sulfuric acid—used in esterifications and to dry gases
- Desiccator materials—calcium chloride, sodium hydroxide, sulfuric acid, phosphorus pentoxide (P_4O_{10})
- Silica gel—used to prevent rust of military and industrial parts; easily regenerated.

- "Dowflake" or similar—this crude calcium chloride recovered as a byproduct of the solvay process. It is used to melt ice and to reduce dust on clay tennis courts. It is injurious to lawns and, if used on roads, can cause severe corrosion to underparts of automobiles.

3.69. Purification of Water

The following are examples of situations which present and future generations must meet in regard to a growing shortage of usable water:

- Population pressures require the development of new sources of drinking water and better conservation of existing supplies.
- The same pressures require the production of more food from existing farm acreage. This requires fertilizers and more water. New arable land must be developed by irrigation of arid regions.
- Every rise in living standards is accompanied by an increase in per capita water consumption for personal cleanliness, private swimming pools and the manufacturing of consumer goods.
- Increased industrialization places constant new strains on water resources. It is not uncommon for a single large plant to equal or exceed the daily water consumption of a city.
- Impurities in water can interfere with certain manufacturing processes or cause premature breakdown of equipment. Many industries invest sizable funds in the chemical treatment of their water supply.

The increasing need for water is being met by experimenting with new techniques such as the following:

- The conversion of sea water to potable water
- Organic monolayers used to reduce evaporation from reservoirs
- Chemical cloud seeding
- Melting of ice on sea water
- Towing icebergs into ports to supplement the existing water supply
- Electrodialysis of sea water; see activity 3.47
- Use of live steam to turn electric generators and the spent steam to provide heat for evaporation, thus reducing the cost of the distilled water
- Ion exchange techniques (presently too expensive for large-scale use) see activities 3.74 and 3.75

See references *3R-21-22* for further information on this topic.

3.70. Coagulation—Absorption

Set up two tall cylinders containing a suspension of muddy water made with common soil, clay or kaolinite. Keep one cylinder as a control. Stir into the other 24 ml. of about 3M $AlCl_3 \cdot 6H_2O$ solution, followed by the addition with stirring of 25 ml. of concentrated ammonium hydroxide. Allow the $Al(OH)_3$ to settle for one-half hour carrying the mud with it. Compare the cylinders. Aluminum sulfate and calcium hydroxide are used commercially.

3.71. Distillation

a. If the laboratory possesses a Barnstead type still, show the internal construction by means of a slide or chart and discuss its operation. Pupils may be assigned to take turns operating the still during the year to keep the laboratory supplied.

b. The following demonstration shows that distillation is not a cure-all for impurities. Set up a conventional laboratory distillation apparatus with a water-cooled condenser. Emphasize that there is no direct contact between the water flowing in the outer jacket and the distillation stream inside. Put tapwater in the distilling flask, then add a soluble salt such as sodium chloride, a suspended material (clay or kaolin), an organic impurity (a few drops of impure kerosene or turpentine) and a dissolved gas (some ammonium hydroxide). Distill about one-half into the receiver. Examine the distillate for impurities. The clarity indicates that the clay has been removed; the organic liquid, nicely purified, is floating on the distilled water, unremoved; a drop of phenolphthalein added to the distillate shows it to contain dissolved ammonia.

A quick conductivity test will show that salt has been removed if compared with the original solution. The class should reach the generalization that volatility determines what will be removed.

The pupils should realize that:

- The purity of distilled water in a chemistry laboratory is affected by gases present in the atmosphere: HCl, NH_3, H_2S, SO_2. All distilled water may contain dissolved CO_2, giving it an acid reaction, but it can be expelled by boiling.
- The longer distilled water stands around, the greater the impurity. If kept in glass, it becomes contaminated with sodium silicate. See activity 3.05.
- Distilled water is not sterile unless specially protected. If exposed to dust, it gradually supports a considerable colony of micro-organisms. Sterile distilled water is not necessarily safe for injections as it may still contain "pyrogens" (fever-producing

agents). A little potassium permanganate is often added to the distilling flask to oxidize such impurities, and the water is then triple distilled in a closed system. The best distilled water is made by passing the steam through a short section of very hot tubing before it enters the condenser. This hot section prevents the existence of a film of water on the inside wall of the tubing that could allow passage of impurities from distilling flask to receiver without vaporization. See reference *3R-23* for additional information.

3.72. Fractional Distillation

The previous activity illustrated the problem of separating volatile substances such as ammonia and water. By collecting the distillate in portions, the separation is improved.

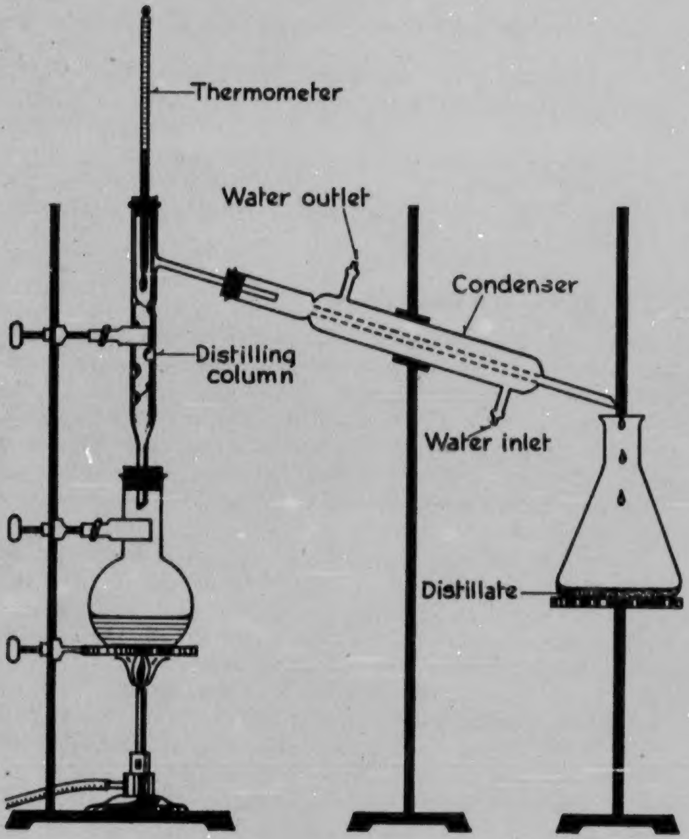
a. Place a mixture of 100 ml. of tapwater and 10 ml. of ethyl alcohol in the distilling flask. Test a small sample of the mixture to see if it will burn. Distill the mixture by heating gently and collect 10-ml. fractions of the distillate in test tubes. Test each fraction to see if it will burn.

Perform the iodoform test on the fractions: Dissolve 10 gm. of iodine crystals in 50 ml. of 3N sodium hydroxide. To 10 ml. of this reagent add several ml. of the filtrate and heat gently in a test tube. A fine yellow precipitate of iodoform, CHI_3, with its characteristic odor of antiseptic indicates the presence of ethyl alcohol.

b. A similar fractionation of 100 ml. of distilled water plus *one* drop of ammonium hydroxide may be performed. Collect the distillate in 5 or 10 ml. portions in test tubes to which a drop of phenolphthalein indicator has been added. Continue until only 40 ml. remains undistilled, then add a few drops of phenolphthalein to the distilling flask. Discuss the effect of refractionating each of these fractions.

c. To illustrate how refractionation may be done in one step, set up a distillation apparatus with thermometer and a distilling column included (see diagram 3.72). Separate a 50-50 mixture of carbon tetrachloride (boiling point 76.8°C.) from toluene (boiling point 110.6°C.) with the aid of the column while a similar mixture is being distilled without a column. Read out the temperature on each apparatus at one-minute intervals to indicate the progress of the separations.

d. Some mixtures cannot be separated even by fractional distillation. These are called constant-boiling mixtures. At a certain concentration hydrogen chloride and water form such a mixture with a boiling point of 108.584 ± 0.004°C. at standard pressure. This is referred to as "constant-boiling hydrochloric acid." Details may be found in a text on quantitative analysis.


Thermometer
Water outlet
Condenser
Distilling column
Water inlet
Distillate

3.72

3.73. Vacuum Distillation

By distillation at low temperatures, delicate organic molecules can be protected from decomposition. *TEACHER DEMONSTRATION ONLY:*

Illustrate the basis of the method by filling a round bottom flask two thirds full of water. Boil a few minutes to expell all air; shut off bunsen burner and stopper the flask; invert the flask and pour cold water over it. The water boils in this near vacuum and will continue to boil as the flask is passed among members of the class. See *Physics Handbook*, activity 2.32. Exhibit apparatus used in vacuum distillation.

3.74. Softening of Water by Ion Exchange

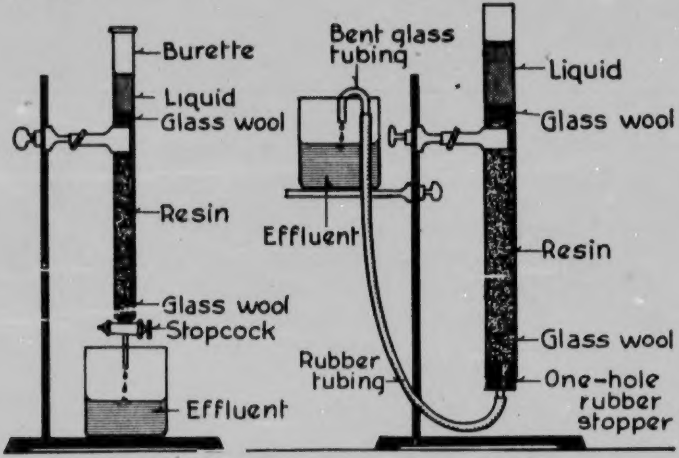
Ion exchange columns for softening water are useful in high school laboratories. The active materials consist of a complex mineral of sodium silico-aluminate or an organic polymer resin which will exchange part of a salt (calcium or magnesium ions) for another (sodium ions) which will make the salt unreactive toward soaps.

A strong solution of common table salt is used to wash out the accumulated calcium or magnesium ions after a period of use and thus regenerate the column. Follow the directions that accompany the apparatus.

Pass hard water made by adding a few crystals of Epsom salts to tapwater through the column. Test the resulting water with soap solution for hardness. The unwanted ions which cause water to be hard are detained by the resin. They have been exchanged for sodium ions which do not cause hardness.

3.75. Using Ion-Exchange Resins

Ion-exchange resins may be obtained at reasonable cost by the pound from supply houses. The following resins are recommended for the experiments described below: amberlite IR-120(H), amberlite IR-4B(OH), and amberlite MB-1. Separate columns should be prepared for each resin.


Burette
Liquid
Glass wool
Resin
Glass wool
Stopcock
Effluent
Bent glass tubing
Effluent
Rubber tubing
Liquid
Glass wool
Resin
Glass wool
One-hole rubber stopper

(1) (2)

3.75

To prepare a column, first pack in a wad of glass wool just large enough and tightly enough so that resin particles will not pass through. Burettes, lamp chimneys or other glass tubing may be used. See diagram 3.75. Using *caution* mix the resin with distilled water in a beaker and allow to stand for at least an hour, preferably overnight. This is a necessary precaution because of the expansion of the resin. *CAUTION: Never add a liquid to a dry column; it may shatter as a result of the expansion pressure.*

Now pour the resin suspension into the prepared column. Excess water will run out and the resin will settle to the bottom. Continue the process until there is enough resin to fill the burette or column to about five inches from the top. Do not allow the water column to drop below the top of the resin at any time.

a. **Cation Exchange.** Use the amberlite IR-120(H) column. This polystyrene sulfonic acid type resin illustrates the exchange of metallic ions for hydrogen. An acid results in the effluent.

Add a 1 percent solution of NaCl to the column and test the resulting effluent for acid content (HCl) by means of the usual indicators.

Pass a dilute solution of the NaOH colored with phenolphthalein through the column. The effluent will be colorless. The above exchanges may be represented by the following equations:

$$\mathrm{NaCl} + \mathrm{H{\cdot}Resin} \rightarrow \mathrm{Na{\cdot}Resin} + \mathrm{HCl}$$
$$\mathrm{NaOH} + \mathrm{H{\cdot}Resin} \rightarrow \mathrm{Na{\cdot}Resin} + \mathrm{HOH}$$

b. **Anion Exchange.** Use the amberlite IR-4B(OH) column; weakly basic amine groups on this resin take anions and give off hydroxide ions.

Pass the dilute HCl which resulted from above through the column and test the effluent for acid content. The liquid will be neutral.

Add a 2 percent solution of $MgSO_4$ to the column and again test the effluent with an indicator. The resulting solution will be alkaline.

c. **Demineralizing Water.** Demonstrate the removal of ions by using the propet column. Prepare 2 percent solutions of nickel (II) sulfate and copper (II) sulfate. Test for the presence of each component of the solution as follows:

- Test for nickel ions—add an alcohol solution of dimethyglyoxime. A red precipitate forms.
- Test for copper ions—add NH_4OH until the precipitate that first forms dissolves to form a deep blue solution.
- Test for sulfate ions—add $BaCl_2$ to obtain precipitate insoluble in HCl.
- Use conductivity apparatus to show that ions in solution conduct the electric current.

Now add the blue copper sulfate solution to the amberlite MB-1 resin. This is a mixture of the other two resins ("mixed bed") and absorbs both anions and cations. A second pass through the column may be necessary. Now test the effluent for copper ion, sulfate ion and for conductivity. Repeat the above process with the green nickel sulfate solution. The composition of the effluent should approximate that of distilled water. Amberlite MB-3 is similar in action, but contains an indicator to show when its capacity has been exhausted.

Explain why a column is used in preference to a batch process of mixing resin and solution in a beaker (multiplicity of stages rather than a single stage).

Mixed bed resins are often discarded when exhausted, but on a commercial scale they can be regenerated by separating the anion and cation resins by flotation (difference in densities), and regenerating each resin with the proper chemical (H_2SO_4 and NaOH). The resins are then remixed and reused.

Ion exchange resins have found application in the preparation of residue-free boiler waters for steam power plants as well as in the recovery and separation of materials from industrial process as well as in the recovery and separation of materials from industrial processes found in streams. By this method penicillin is separated from the broth in which it is grown (see reference *3R-24*).

Area 3 Referencos

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NOTES

AREA 4

Nonmetals

4.01. Location of Nonmetals in the Periodic Table

Use the periodic table as a point of reference to illustrate the chemical and physical properties of nonmetals (see pages 334-335). Relate to activities 2.20, 2.21 and 2.22.

Have pupils locate the nonmetals in the periodic table. Show that they represent about 20 percent of the elements. Emphasize that there is no hard and fast line between metals and nonmetals, as shown on many charts, but a more or less gradual transition. Any element near the line may have a mixture of metallic and nonmetallic qualities. This sometimes shows up more readily in compounds than in the element itself, as in the case of aluminum.

4.02. Some Physical Properties of Nonmetals

a. Make a display of some common nonmetals usually found in the laboratory such as: bromine, iodine, sulfur, phosphorus, silicon and carbon. Have the pupils list the physical properties to bring out the lack of common characteristics among nonmetals. In the listing, nonmetals such as oxygen, nitrogen and chlorine should be included. Develop the understanding that most nonmetals are either gases or brittle solids under ordinary conditions. See reference *4R-1* for additional material.

b. From the following list, select properties for discussion and comparison:

Boiling point
Color
Conductivity for heat
Conductivity for electricity
Crystal form
Density
Ductility
Hardness
Heat of combustion
Heat of formation
Heat of fusion
Heat of vaporization
Luster
Malleability
Melting point
Odor
Solubility
Tensile strength

c. Melt sulfur to show the relatively low melting point characteristic of nonmetals. Attempt to conduct a current through the molten element. Repeat, using iodine.

d. Ignite a piece of charcoal, holding one end in the hand to show poor conductivity of heat. Repeat with a lump of sulfur. Contrast with the conductivity of metals.

4.03. Some Chemical Properties of Nonmetals

Phosphorus exhibits the general properties of the nonmetals. Some of the more important chemical properties are:

- Reacts with both metals and nonmetals
- Forms acids
- Has variable valences
- Often forms covalent bonds
- Is often toxic

Phosphorus has an interesting history (see reference *4R-1*).

CAUTION: In all experiments with phosphorus, the phosphorus residue should be completely burned or kept totally submerged in water until it can be safely destroyed.

a. TEACHER DEMONSTRATION ONLY: Ignite a little *red* phosphorus in a deflagrating spoon and lower while still burning into an 8-ounce gas bottle containing 1 inch of water. Allow time for some of the oxide to react with the water, or stopper and shake. Show (with litmus or other indicator) that the water now contains an acid.

b. TEACHER DEMONSTRATION ONLY: Show that phosphorus reacts with metals to form salts. Place a small amount (size of a pea) of *red* phosphorus in the bottom of a test tube. Form a loose ½-inch plug of asbestos fibers or pyrex glass wool about 3 inches above the phosphorus and add a ¼-inch layer of aluminum or magnesium metal powder. For an alternate demonstration substitute for the metal a ½-inch layer of zinc powder or of calcium turnings, or a 1-inch layer of steel wool. Cover with another plug of asbestos or glass wool.

Heat the red phosphorus with a burner until white fumes appear. The metal should now be heated; the magnesium to ignition, and the other metals to a red heat. On cooling, the phosphide may be removed. Treatment with water yields impure phosphine which may ignite spontaneously.

4.04. Formation of Salts and Acids

a. Salts.

(1) Cautiously sprinkle finely divided zinc dust or antimony dust

into a bottle of chlorine. A vigorous reaction will occur.

(2) Place some powdered zinc and crystalline iodine in a dry evaporating dish. Add a drop or two of water with a medicine dropper. The combustion is immediate, producing zinc iodide.

b. Acids.

(1) Burn sulfur in a bottle full of oxygen to produce sulfur dioxide. Use a deflagrating spoon. Pour 50 ml. of water into the bottle and shake. Test the solution with litmus paper to show the acid reaction.

(2) Repeat the procedure using charcoal. Show that the resulting solution is acidic.

(3) *TEACHER DEMONSTRATION ONLY:* Nonmetals may combine directly with hydrogen to form acids. Demonstrate that hydrogen will burn in chlorine to produce hydrogen chloride gas. This is combined with water to form hydrochloric acid. Hold a lighted taper to a mixture of hydrogen and chlorine contained in a 100-ml. bottle.

CAUTION: A violent reaction occurs. Add water, shake the bottle and test for the hydronium ion with blue litmus.

4.05. Identification of Anions

a. Illustrate the general character of anion analysis by performing a few typical tests.

(1) **Formation of a Precipitate.** Add silver nitrate solution to a solution containing chloride ions.

(2) **Formation of a Gas.** Add a strong sulfuric acid solution to sodium nitrite crystals in a test tube.

(3) **Change of Color.** Add potassium permanganate solution to a solution containing a sulfite salt to which a little acid has been added.

b. When pupils have had laboratory experience in performing tests, issue an unknown to be tested for the presence of Br^-, I^-, CO_3^{--}, SO_4^{--}, SO_3^{--}, OH^-, NO_3^-, and NO_2^-.

4.06. Elements Forming Amphoteric Hydroxides

Besides the definite metals and nonmetals there are elements with some of the properties of each. The diagonal line on the periodic table separating metals and nonmetals actually represents a *zone of gradual transition* of properties (see page 334-335). Elements on or near the line may be "metalloids" or elements which form amphoteric hydroxides. Refer to activities 2.20 and 2.21. See also reference *4R-3*.

a. Physical Properties. Point out such physical properties as the following:

- *Silicon*—shows metallic luster, is a fair conductor
- *Arsenic*—occurs in two forms, one "nonmetallic," the other "semimetallic" in appearance; is a fair conductor
- *Tellurium*—has a metallic appearance, is brittle and is a poor conductor
- *Astatine*—behaves generally as a metal
- *Germanium*—is metallic, has flaky, brittle crystals; is not a very good conductor of heat or electricity.

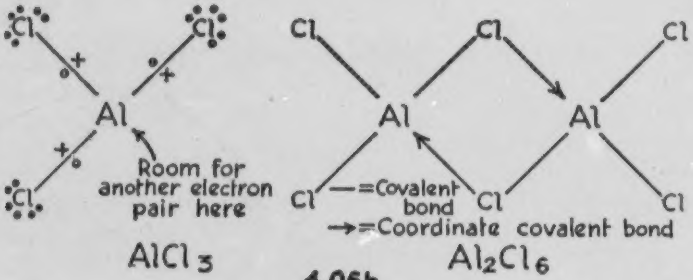
Point out other elements farther removed from the dividing line, such as:

- *Graphite*—has some luster, is a good conductor of electricity
- *Iodine*—has some luster
- *Bismuth*—is brittle, is a poor conductor of electricity
- *Selenium*—occurs in two forms, gray form exhibits photoconductivity
- *Tin*—has metallic form at room temperature, is a powder at low temperatures
- *Germanium*—is a semiconductor
- *Silicon*—is a semiconductor

b. Chemical Properties.

Aluminum exhibits a typical metallic appearance, good conductivity and is high on the electromotive series, but is distinctly metalloid.

(1) Set up two beakers of water. Place some sodium chloride in one, pointing out that it is an ionic compound and the water merely separates the ions that are already present in the crystal. Exhibit some *anhydrous* aluminum chloride. It is a rather amorphous powder. Using *caution*, place a small spatula full of the aluminum chloride in the second beaker. It reacts violently with the water. The temperature of


Cl
Cl
Al
Cl
Room for another electron pair here
AlCl3
Cl
Cl
Cl
Al
Al
Cl
Cl
Cl
—=Covalent bond
→=Coordinate covalent bond
Al2Cl6

4.06b

the water rises, as a thermometer will show. Point out that aluminum chloride is a covalent molecule with the actual formula Al_2Cl_6, as determined from molecular weight analysis of the vapor (see diagram 4.06*b*). The water in this case *converts* it into ions, with partial decomposition into HCl and Al_2O_3. The Al^{+++} ion exists in water as a complex, $Al(H_2O)_6^{+++}$, and when crystallized from water forms a hydrated crystal ($AlCl_3 \cdot 6H_2O$). Show a sample of such crystals to the class. *Note:* Keep the bottle of anhydrous aluminum chloride tightly stoppered when not in use to prevent decomposition due to water vapor in the air.

(2) Set up two dry beakers in a tray to catch overflow, with each containing about 5 gm. of granular (not powdered) aluminum metal. To one beaker add about 25 ml. of 6N hydrochloric acid; to the other, 25 ml. of about 6N sodium hydroxide. Observe the manner of reaction for a few moments noting that the base is slower in removing the oxide layer on the metal. Ignite the bubbles of hydrogen in each beaker. Discuss the two different salts that form:

$$2Al + 6HCl \rightarrow 2AlCl_3 + 3H_2$$

$$2Al + 2Na0H + 2H_20 \rightarrow 2NaAl0_2 + 3H_2$$

Exhibit a sample of commercial drain cleaner. Show that it is lye mixed with granules of aluminum so that the hydrogen evolved will help to break up the matter clogging the drain. Discuss the importance of keeping such substances away from aluminum utensils.

(3) Point out that other metals form chloride compounds that are covalent liquids, such as: $SnCl_4$, $PbCl_4$, $AsCl_3$, $SbCl_5$ and $TiCl_4$. Look up their unusual properties in a handbook.

4.07. Amphoteric Hydroxides

a. Discuss the following formulas to indicate that acids and bases have different structures, then ask the class to suggest names for these acids and their salts.

Formula as Base	*Formula as Acid*
$Al(OH)_3$	H_3AlO_3 (or $HAl0_2$ + H_20)
$Zn(OH)_2$	H_2ZnO_2
$Pb(OH)_2$	H_2PbO_2

b. Show that the substances listed in *a* above can act as acids or bases depending upon their environment.

(1) Prepare a suspension of aluminum hydroxide by adding a little aluminum chloride or aluminum sulfate to water, followed by a few drops of dilute sodium hydroxide solution. Divide this among three test tubes. Keep the center tube for reference. Add concentrated HCl

to one tube and a strong solution of sodium hydroxide (6N) to the other. The precipitate dissolves in both cases, forming $AlCl_3$ and $NaAlO_2$ respectively.

(2) Repeat as above, starting with $ZnCl_2$. The salts in this case are $ZnCl_2$ and Na_2ZnO_2. Show that the structure of the hydroxide is H—O—Zn—O—H, and where it ionizes depends upon the electron-attracting or electron-repelling ability of the central atom. Compare with the action of H—O—Ca—O—H and H—O—(SO_2)—O—H.

(3) Prepare a dilute solution of $Pb(NO_3)_2$. Add a dilute solution of KOH dropwise until white $Pb(OH)_2$ precipitates. Place in three test tubes, and keeping the middle tube as a control, add nitric acid to one tube (soluble $Pb(NO_3)_2$ reforms), and approximately 3N KOH solution to the other (soluble K_2PbO_2 forms).

(4) Add a few drops of $Pb(NO_3)_2$ solution to water. Then add a few drops of $K_2Cr_2O_7$ solution which will form the precipitate, $PbCrO_4$. This precipitate is soluble in HCl, forming orange $PbCr_2O_7$, and it is soluble in 3N NaOH, forming yellow Na_2PbO_2.

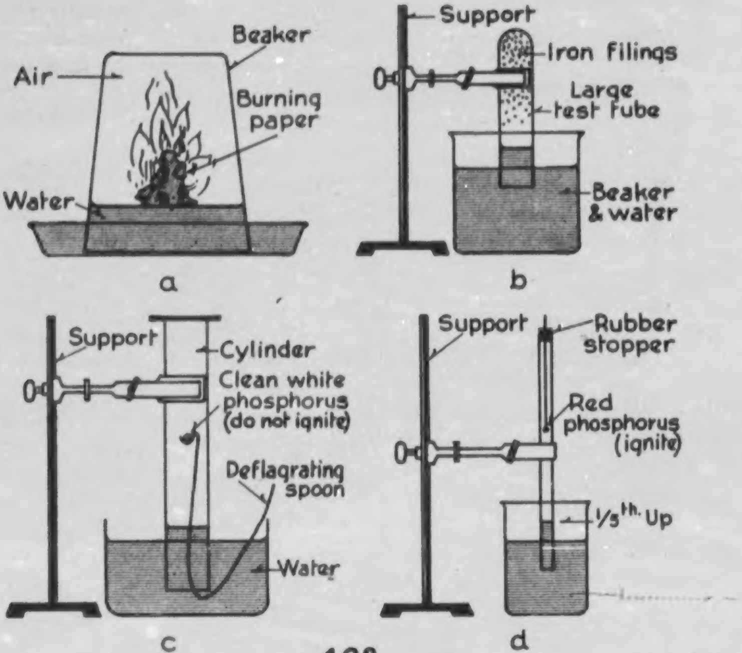
4.08. Oxygen in the Atmosphere

a. Crumple a piece of newspaper into a ball, float it in a dish of water, ignite the paper, and immediately cover with a beaker (see diagram 4.08*a*). Pupils will observe the water rising in the beaker as it cools. Determine if a green plant or an animal would produce a similar effect.

b. Pupils may perform a quantitative analysis of oxygen in the atmosphere by one or more of the following methods:

(1) Moisten the inside of a 200-ml. test tube with dilute acetic acid. Add enough iron filings to form a thin layer of iron on the inside of the tube, as shown in diagram 4.08*b*. Invert the tube over water and leave it undisturbed overnight. An examination the next day will reveal that most of the iron had rusted and the water had risen into the test tube. Measure the volume of oxygen consumed, as indicated by the rise in water level. Compare this rise to the original volume of air in the test tube and calculate the percent of oxygen in the air. *Note:* Acetic acid is used to moisten the tube instead of water since it exhibits a catalytic reaction and hastens the oxidation of the iron. Water alone may be used.

(2) Bend a deflagrating spoon in the shape of a "*V*" as indicated in diagram 4.08*c*. Place a piece of white phosphorus in the ladle and let the apparatus stand overnight. The phosphorus consumes the oxygen and the water level rises. It is necessary to allow sufficient time for the phosphorus pentoxide to dissolve before taking a final reading.


Beaker
Air
Burning paper
Water
a
Support
Iron filings
Large test tube
Beaker & water
b
Support
Cylinder
Clean white phosphorus (do not ignite)
Deflagrating spoon
Water
c
Support
Rubber stopper
Red phosphorus (ignite)
1/5th. Up
d

4.08

CAUTION: White phosphorus may cause severe skin injuries. Handle with forceps only. Red phosphorus reacts more rapidly (see diagram 4.08*d*), but combustion may not be complete.

(3) Amateur photographers may be familiar with the manner in which a tray of developer will darken on exposure to air. This is due to oxidation of the reducing agent in the developer, a reaction which is generally catalyzed by alkaline conditions. Fit the top of a 50-ml. burette with a rubber stopper. Determine what volume of 5 percent sodium hydroxide solution should be added to the burette so that just 50 ml. of air will remain. Add the required amount of base, then quickly dump in 0.5 gm. of powdered pyrogallic acid, stopper, and shake. Place the tip of the burette under water and open the pinchcock. Note how the water rushes in to replace the oxygen. Allow the burette to cool, then raise or lower the burette so that the water level is the same inside and outside to bring the remaining gas to room pressure. Measure the residual gas and subtract from the original value, 50 ml., to find the volume of oxygen.

c. Variations in the composition of the atmosphere are beginning to cause some concern. Two variations under study are the carbon dioxide content and the O^{16}—O^{18} ratio. A pupil may wish to report to the class on this problem (seé references *4R-4-5*).

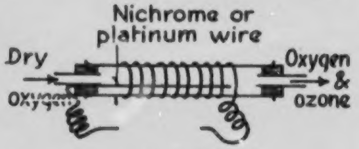
4.09. Ozone

a. Ozone is a powerful oxidizing agent exceeding all ordinary chemicals except fluorine in its oxidation potential. Display advertisements from chemical magazines to illustrate its growing use as an industrial oxidant. (See references *4R-6-8* for detailed accounts.)

b. Generate a little ozone by one of the following techniques and observe its odor and properties:

(1) See diagram 4.09*b*. The platinum wire, which is connected to one of the secondary terminals of an induction coil, is held axially by the cork and inlet tube. The other terminal of the induction coil is connected to a wire wrapped around the outside tube, which is about ¾ inch x 8 inches.

The yield is adequate to note the odor and to demonstrate the oxidizing properties of ozone. A nichrome wire may be used in place of the platinum.



4.09b

(2) Small " ozone-makers " employing lamps that emit ultraviolet light are on the market for home use. Compare their operation to the action of sunlight on the upper atmosphere. There is a layer rich in ozone about 20 miles above the earth. Lightning produces a similar effect and causes the air to " smell sweet " after a storm; in higher concentrations ozone has a pungent " electrical " odor (see reference *4R-4*).

4.10. Atomic Oxygen

At an altitude above 60 miles, large though dilute amounts of dissociated oxygen are present due to the reaction:

$$O_2 \xrightarrow{\text{solar energy}} 2\,O$$

This has created interest in utilizing the reverse reaction as an unlimited energy source for high altitude rockets (see reference *4R-4 and 9*). Ask a pupil to report on the current state of this research.

4.11. Commercial Preparation of Oxygen

a. Prepare a display of pictures and brochures on the production of oxygen by the fractional distillation of liquid air ("air reduction"). This process grew during World War I when plants capable of producing several tons of oxygen a day were constructed. At that time the principal use was for oxy-acetylene welding. Modern plants produce over 100 tons of liquid oxygen ("lox") per day.

A new cryogenic process for removing oxygen from air is under development which requires pressures of only 85 lbs./in.^{2}, compared to present equipment operating at about 2,500 lbs./in.^{2}. Improved techniques in producing low temperatures are the heart of the process, which is expected to reduce costs about 25 percent. See reference *4R-10* for additional information which may be helpful for pupil reports.

Note: Do not perform any demonstrations involving liquid air. Liquid nitrogen demonstrations are to be performed only where proper equipment and expert handling can be assured.

4.12. Laboratory Preparations of Oxygen

a. While preparation from potassium chlorate is not dangerous by itself, the possibility of serious accident is present if any oxidizable material gets into the reaction mixture. It is strongly urged that other preparations be substituted, and potassium chlorate utilized in a *TEACHER DEMONSTRATION ONLY. CAUTION: Manganese dioxide obtained from dry cells contains powdered carbon and should never be used.*

b. Oxygen can be prepared in small amounts by heating silver oxide, lead dioxide (PbO_2), potassium permanganate, red lead (Pb_3O_4), and mercuric oxide at suitable temperatures. *CAUTION: When working with mercury compounds always use the hood.*

c. If direct current is available, electrolysis of water is an excellent pupil preparation. See reference *4R-11.* A 2M sodium sulfate solution is preferable to sulfuric acid as the electrolyte.

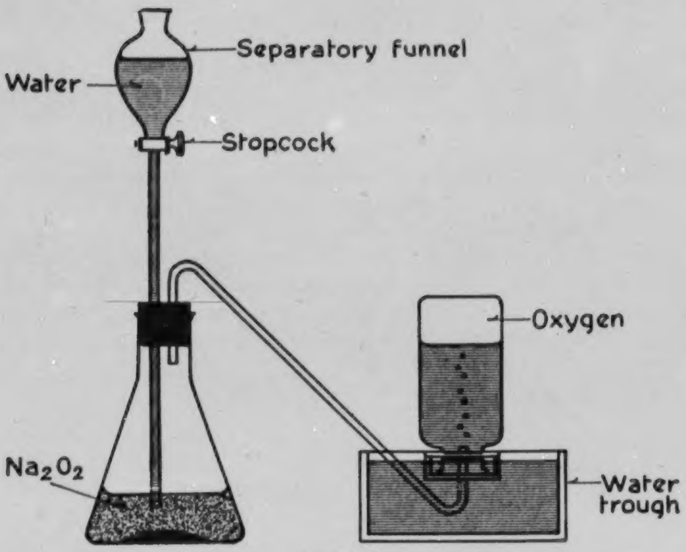
d. Oxygen may also be prepared from peroxides. Hydrogen peroxide once removed from the original container should not be returned because of the risk of contamination and subsequent decomposition of the remainder of the solution. If this precaution is observed, the standard drugstore peroxide is reasonably stable in storage.

Thirty percent solutions of H_2O_2 are available from chemical supply houses. This is a dangerous oxidizing agent and should not be distributed to pupils because it can produce serious skin burns. The teacher should carefully dilute the mixture to a 6 percent solution.

(1) Place about 5 ml. of a 6 percent hydrogen peroxide solution in a 15-ml. test tube. Add one or two very small crystals of potassium permanganate. The manganese is rapidly reduced to yield manganese dioxide. The manganese dioxide is produced in the form of a fine brownish dispersion which is a very active catalyst for the decomposition of the hydrogen peroxide. By proper dosing with the permanganate, one can readily obtain a steady decomposition lasting for several minutes during which the glowing splint test and other tests may be used to demonstrate the properties of the oxygen released. If too much permanganate is used, the decomposition occurs rather quickly so that there is little time for demonstrating the properties of the oxygen. No hazard exists with 6 percent hydrogen peroxide, regardless of the amount of permanganate used.

(2) For somewhat larger quantities of oxygen, it is convenient to place about 25 ml. of 6 percent hydrogen peroxide in a 250-ml. Erlenmeyer flask. To this may be added a few small crystals of potassium permanganate to a total of 50 or 100 milligrams (size of a match head). A steady stream of oxygen will be generated. This may be led to a pneumatic trough and collection bottles by means of a one-hole stopper and tubing. Hydrogen peroxide of 6 percent strength will release about 20 times its own volume of oxygen so that a 25 ml. portion will produce 500 ml. of pure oxygen. This procedure avoids all of the hazards connected with the usual procedure of heating a chlorate with a catalyst. The dilute peroxide solution is virtually harmless, and no heating is required. The apparatus illustrated in diagram 4.12*d* may be used, placing the potassium permanganate in the flask and the hydrogen peroxide in a dropping funnel or separatory funnel.

(3) Arrange a dropping funnel in a 1,000-ml. Erlenmeyer flask as shown in diagram 4.12*d*. Place 50 gm. of fresh sodium peroxide in the flask. The yield of oxygen is controlled by the rate at which water is added from the dropping funnel. Collect oxygen by water displacement.



4.12d

4.13. Oxidation

The history of oxygen and the theory of oxidation is rich in materials, especially regarding the nature of the scientific method. Some activities are suggested below. See also references *4R-13-17*.

a. Demonstrate the liberation of oxygen by heating mercuric oxide (one of Priestley's methods).

b. Review the demonstration similar to Lavoisier's experiment described in activity 1.33*a*.

c. Roll some steel wool into a tight ball that will fit into a crucible. Weigh carefully and heat over a bunsen burner. To increase the extent of oxidation blow a stream of air into the hot steel wool through a glass tubing straw. There is a noticeable gain in weight.

d. Demonstrate rapid oxidation with pure oxygen by burning small samples of magnesium or calcium in a gas bottle filled with oxygen. Add a little water containing phenolphthalein indicator, stopper and shake to show the formation of bases. Repeat using nonmetals such as carbon, sulfur or red phosphorus and litmus or other suitable indicator to show the formation of acids. These reactions should preferably be done as pupil laboratory exercises.

4.14. Spontaneous Combustion

Discuss the requirements for spontaneous combustion: (1) a slow oxidation process, (2) an insulator, and (3) a material with relatively low kindling temperature.

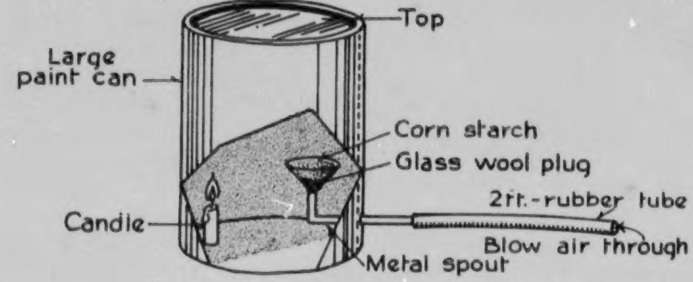
TEACHER DEMONSTRATION ONLY: Cautiously dissolve a piece of white phosphorus about the size of a pea in 10 ml. of carbon disulfide. Prepare only as needed; do not store. *CAUTION: This mixture causes painful burns; use hood because of nasty odor.* Crumple a piece of newspaper and place on an asbestos square or in a porcelain dish. Pour some of this solution onto the newspaper. As the solvent evaporates, the phosphorus is exposed to oxygen. The paper serves as an insulating agent permitting kindling temperature to be reached.

4.15. Dust Explosions

a. Illustrate the effect of particle size upon the rate of combustion. Hold an iron nail in the bunsen flame with a forceps. Then sprinkle iron filings into the flame from a salt shaker. Repeat with other powdered metals.

b. Illustrate the effect of particle dispersion by comparing the burning of iron filings piled in a cone on an asbestos square with those sprinkled into the flame.

c. TEACHER DEMONSTRATION ONLY: See diagram 4.15c for apparatus to demonstrate the effect of a dust explosion by blowing lycopodium powder, cornstarch or flour into a confined area containing a flame. Call attention to the factors involved in rapid oxidation: (1) a finely divided combustible material, (2) oxygen and (3) a source of heat.



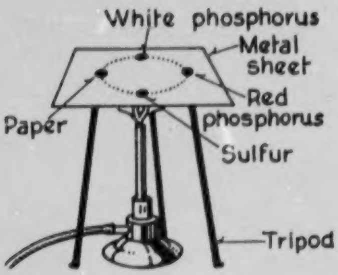
4.15c

Demonstrate this exercise, first, with the lid off the can and, second, with the lid on. *CAUTION: Keep head away from mouth of can, and do not perform the demonstration under a light fixture.*

4.16. Kindling Temperature

Demonstrate that heating to the kindling temperature is necessary in order for burning to occur. Make a copper cross from two strips of heavy-gauge copper. Place pieces of red phosphorus, yellow phosphorus, sulfur and paper on the ends. *CAUTIONS: Only the teacher should use yellow phosphorus. Use the hood.* Heat the cross in the center and note different times at which combustion occurs.

This may be similarly performed by using a square piece of metal (iron). Place substances in a circle some distance from the center. Support on a tripod and apply heat from the underside of the metal. Note relative kindling point of each substance (see diagram 4.16).



4.16

4.17. Fire Extinguishers

a. Soda-Acid Type. *TEACHER DEMONSTRATION ONLY:* Make a soda-acid type fire extinguisher by fitting a widemouthed bottle with a one-hole rubber stopper containing a short delivery tube. Nearly fill the bottle with a saturated solution of sodium bicarbonate. Place a small test tube containing sulfuric acid (1:8) in the bottle, and stopper the bottle firmly. Invert and direct the contents against a fire made in the laboratory sink. *Note:* Once the reaction begins, it cannot be stopped.

b. Foamite Type. Prepare a test tube full of a concentrated alum solution, containing about ¼ gm. of powdered white of an egg (albumin). Prepare a test tube full of a saturated solution of sodium bicarbonate at the same time. Pour 10 ml. of kerosene into an evaporating dish and ignite it. Hold both of the prepared test tubes over the side of the evaporating dish, and pour their contents into the dish so that both solutions mix before falling upon the surface of the burning liquid. The flames will be extinguished within a few seconds.

4.18. The Occurrence and History of Hydrogen

Discuss the occurrence of hydrogen, bringing out the following points of interest:

- Some hydrogen occurs in the free state, especially in the upper atmosphere.
- Hydrogen forms more compounds than any other element; most of these are organic.
- The crust of the earth is 1 percent hydrogen by weight, but 16 percent by number of atoms.
- A great quantity of hydrogen is present in certain rocks and clays; for example, gypsum ($CaSO_4 \cdot 2H_2O$).
- Our sun is 30 percent hydrogen; the universe is primarily hydrogen.
- Hydrogen is the lightest element.
- One out of every 5,000 hydrogen atoms is twice as heavy; this is called *deuterium*.
- One out of every 10^{17} hydrogen atoms is three times as heavy and radioactive. This is natural tritium, produced by cosmic rays in the upper atmosphere at the rate of six atoms per square centimeter of the earth's surface per minute. Every rainfall contains some of it (see reference *4R-18)*.

Discuss the role of the following men in the history of hydrogen:

- Lavoisier
- Cavendish
- Dewar
- Urey
- Teller

4.19. Hydrides

References *4R-19-20* contain information on relatively recent uses of hydrides.

Metallic hydrides are generally unstable, and their preparation is *not recommended.*

4.20. Commercial Preparations of Hydrogen

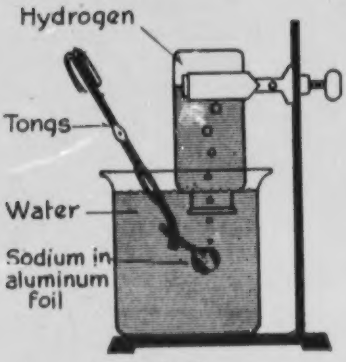
It is well to stress that production of hydrogen by electrolysis of water is too expensive except where electric energy is unusually cheap. Other commercial preparations include:

- Reduction of water by hot carbon
- Reduction of water by hot scrap iron
- Destructive distillation of coal
- Cracking of methane
- Electrolysis of brine
- Reaction involving crude oil, oxygen and water

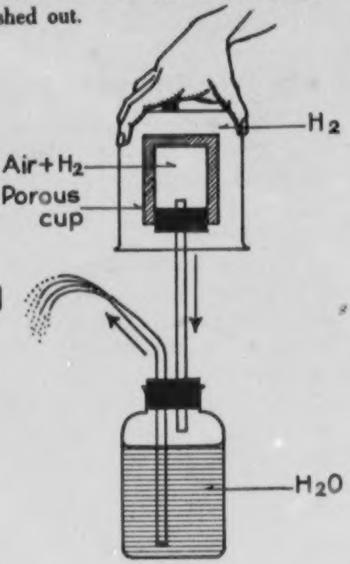
Preparations of hydrogen from steam are instructive but time consuming and balky. They may be demonstrated during a pupil laboratory period as a side exhibit.

4.21. Laboratory Preparations of Hydrogen

a. All pupils should have the opportunity to prepare hydrogen by reaction of zinc with hydrochloric acid. Stress the value of a safety valve (thistle tube) in *all* gas reactions. Bunsen burners should not be lighted until hydrogen has been collected in bottles and the generators have been taken apart and washed out.



4.21d



4.22a

b. Pupil preparation by electrolysis is highly desirable. A simple inexpensive apparatus has been designed, see reference *4R-11*. In this case quantities, such as volume, weight and number of electrons involved in the reaction, should be stressed.

c. Later in the course the preparation from the reaction of a calcium chip with water is instructive. In this case, the activity series of the metals should be stressed.

d. It is instructive to have half the class prepare hydrogen with aluminum *pellets, not powder*, and 6N sodium hydroxide in an apparatus identical to that being used for zinc plus acid. The teacher should test the quantities used beforehand to adjust them to the size of the generators. Once started, this reaction becomes vigorous.

Instruct the other half of the class to wrap a small piece (no larger than the size of a pea) of sodium in aluminum foil to make it easier to manage, puncture the foil in a few places with a pin to allow the water to contact the sodium and collect as in diagram 4.21*d*.

e. Small pieces of sodium, potassium and lithium may be reacted with water in a petri dish placed on the overhead projector. This method insures safety, clarity and a dramatic effect. Repeat, using water to which a little phenolphthalein has been added. *Note:* Sodium is now commercially available in the form of convenient spheres 1/16 to ¼ inch in diameter.

4.22. Properties of Hydrogen

a. **Diffusibility.** Illustrate the ability of hydrogen molecules to pass through openings in a porous clay cup (see diagram 4.22*a*).

b. **Combustibility.** Make a stock soap solution as follows: Cut 25 gm. of pure castile or palm oil soap into thin shavings and dissolve in 200 gm. of distilled water. When solution is complete, add 100 gm. pure glycerine and mix thoroughly. Upon standing, the liquid becomes clear at the bottom. Remove this clear portion with a siphon and store for use. It will keep indefinitely.

Using this soap solution, pass hydrogen from a generator into soapy water forming large hydrogen-filled soap bubbles. Ignite the bubbles as they rise through the room. A noisy but safe explosion will occur.

c. **Reducing Ability.** *TEACHER DEMONSTRATION ONLY:* Place approximately 5 gm. of copper oxide (wire form) in an ignition test tube and arrange the apparatus as shown in upper diagram 4.22*c*. *CAUTION: Make sure all connections are tight. During the demonstration the teacher should wear safety goggles and the pupils should view the activity only from a distance. Allow the hydrogen generator* *to run long enough to expel all the air from the apparatus before lighting the bunsen burner.*

Although 5 gm. of CuO is suggested, the teacher will have to vary the amount as experience demands. If the teacher prefers, a U-shaped drying tube can be substituted for the one-bulb drying tube.

Record the following data:

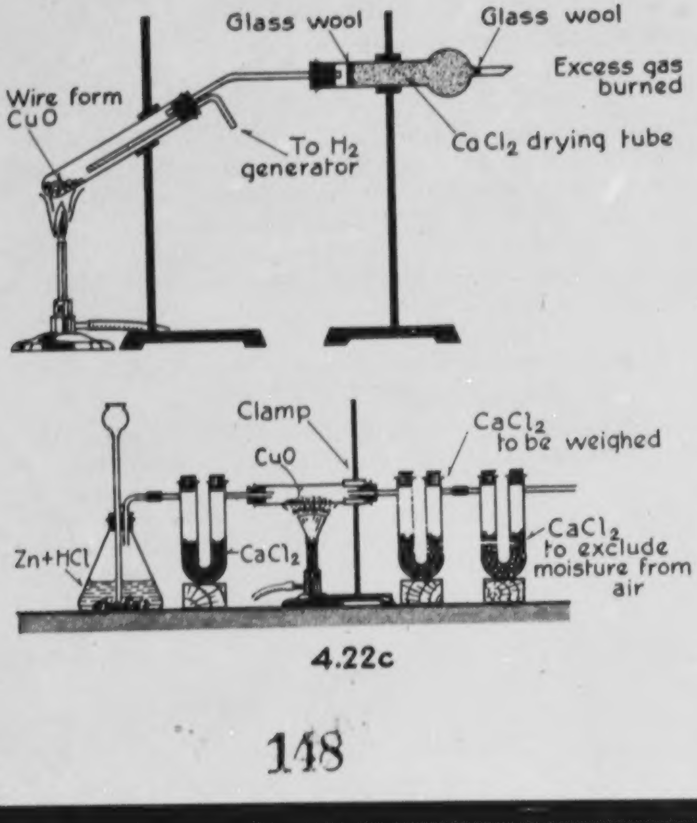
(1) Weight of ignition tube + CuO before heating ________ gm.
(2) Weight of ignition tube + contents after heating ________ gm.

Weight of oxygen removed from CuO (1) — (2) ________ gm.

(3) Weight of drying tube + contents after heating ________ gm.
(4) Weight of drying tube + anhydrous $CaCl_2$ before heating ________ gm.

Weight of H_2O formed (3) — (4) ________ gm.

The loss of weight of the copper oxide, the gain in weight of the contents of the drying tube, and the appearance of the characteristic reddish color of copper in the ignition tube are indications that the black copper oxide has been reduced by hydrogen.


Glass wool
Glass wool
Excess gas burned
Wire form CuO
To H2 generator
CaCl2 drying tube
Clamp
CuO
CaCl2 to be weighed
Zn+HCl
CaCl2
CaCl2 to exclude moisture from air

4.22c

Have pupils determine the amount of water that should have been produced during the reduction process. Compare their results with the difference in weight of the contents of the drying tube before and after the reduction of copper oxide.

An alternate setup is illustrated in lower diagram 4.22c. The hydrogen generator should be kept away from an open flame and covered with a cloth towel during the demonstration.

4.23. Uses of Hydrogen

Discuss some of the following important uses of hydrogen:

- Production of ammonia by the Haber process, which is the single greatest use
- Production of methane from carbon monoxide
- Hydrogenation of unsaturated compounds in gasoline in order to reduce formation of sticky resins in storage
- Hydrogenation of animal and vegetable oil to remove double bonds which are points where bacteria may attack
- Hydrogenation in cell metabolism in plants and animals
- Production of synthetic organic compounds
- Economic recovery of low grade ores of cobalt, nickel and tungsten
- Oxy-hydrogen welding torches to produce high temperatures and to keep metals free from contact with carbon
- One of a mixture of fuels for rocket engines.

A fuel cell operating with hydrogen and oxygen has been proven feasible. Hydrogen and oxygen create electricity directly by reacting with each other to form water. This is the reverse of the electrolysis of water. See reference *4R-21.*

4.24. Preparation, Properties and Uses of Hydrogen Peroxide

a. Preparation. The modern method of producing hydrogen peroxide is by the electrolysis of a strong solution of sulfuric acid. It may be prepared by the older method in the laboratory as a pupil exercise.

Place 5 gm. of barium peroxide in a beaker. Stir 3 gm. of concentrated sulfuric acid into 100 ml. of cool water in a beaker or flask, and cool the resulting dilute acid to 0°C. or below by placing it in a jar containing cracked ice (or snow) and salt mixture. Mix the cold acid and the barium peroxide. Then add powdered barium carbonate slowly to this mixture until no more bubbling is evident. The barium carbonate will react with any excess acid. Filter the mixture. The filter paper holds barium sulfate and a little barium carbonate. The filtrate contains hydrogen peroxide in a dilute solution suitable for tests.

b. Properties. The following illustrate the oxidizing properties of hydrogen peroxide:

(1) Mix a tiny pinch of starch with a crystal of potassium iodide in a test tube half filled with water. Add hydrogen peroxide solution and look for a color change which indicates that the iodide has been oxidized to iodine.

(2) Pour a little ferrous sulfate solution into a test tube containing 5 ml. of ammonium hydroxide and note the color of the ferrous hydroxide precipitate formed. Take the same amount of ferrous sulfate as before, add a little hydrogen peroxide, and mix the liquids. Then add ammonium hydroxide and note the color change which indicates the presence of ferric hydroxide.

(3) Add hydrogen peroxide to a test tube half full of water saturated with hydrogen sulfide. Note the formation of sulfur.

(4) Write a message on white paper with colorless lead acetate solution and expose it to H_2S fumes; black PbS forms. Wipe with a sponge moistened with H_2O_2. The writing disappears, forming white $PbSO_3$. This is the technique used in restoring darkened oil paintings.

To demonstrate the bleaching property of H_2O_2, add a few crystals of borax to a solution of hydrogen peroxide to make it basic. Put a piece of colored woolen cloth into the beaker and boil for about 15 minutes. Compare the color with a sample of the wet unbleached cloth.

c. Uses. Discuss the industrial applications of hydrogen peroxide, where it is used as the 100 percent liquid in tank car quantities. Have a student interested in rocket research report on its use as an oxidant. It is also used to propel torpedoes, and to drive rocket pumps for liquid fuels.

4.25. The Halogen Family

The occurrence and properties of the halogens are related to their positions in the periodic table (see pages 334-335 and activities 2.20 and 2.21).

a. Occurrence. Emphasize that the halogen elements are too active to be found free in nature. Summarize the sources:

- *Fluorine*—CaF_2; fluorspar and fluorite
- *Chlorine*—NaCl; halite, sea water and brine wells
- *Bromine*—$MgBr_2$ and NaBr from sea water

- *Iodine*—$NaIO_3$, kelp and KI
- *Astatine*—Radioactive artificial element prepared by the bombardment of bismuth with alpha particles (see reference *4R-22*)

b. **General Properties.** Prepare a chart comparing the properties of the halogens as in the chart below.

THE HALOGEN FAMILY

Element	Symbol	at. wt.	at. No.	Electronic Structure	Color and Form	Melting Point	Boiling Point	Sodium Halide	Halogen Acid
Fluorine	F	19.00	9	2-7	Pale yellow gas	-223°C	-187°C	NaF	HF
Chlorine	Cl	35.46	17	2-8-7	Greenish yellow gas	-101.6°	34.6°	NaCl	HCl
Bromine	Br	79.92	35	2-8-18-7	Reddish brown liquid	-7.3°	58.7°	NaBr	HBr
Iodine	I	126.9	53	2-8-18-18-7	Grayish black lustrous solid	113.5°	184°	NaI	HI
Astatine	At	(210)	85	2-8-18-32-18-7	Synthesized in 1940. Little is known about its properties. The only halogen without a stable isotope.				

Other properties that may be compared are:

- Valences
- Activity
- Heats of formation of the binary acids
- Atomic radii
- Nuclear radii

4.26. Uses of Fluorine and Its Compounds

Widespread interest in fluoridation of water to prevent dental caries has brought this element to public attention (see references *4R-23-24*), but it has always had important uses and new uses are being discovered. Emphasize the exceptional nature of fluorine chemistry as being due to its small atomic radius resulting in greater control of the orbital electrons. Suggest the following topics for reports and discussions:

- Fluorine gas as an oxidizing agent in the laboratory and in fluorine bomb calorimetry (see reference *4R-25*)
- Fluorine gas as an oxidant for rockets
- Fluosilicic acid, an important byproduct of phosphate production, used in water treatment (see reference *4R-24*)
- Plastics which are highly inert, heat resistant and virtually unbreakable (tetrafluoroethylene resins)
- Separation of uranium isotopes
- Copper-clad plastics used for printed circuits

- Refrigerating liquids largely of the dichlorodifluoromethane type
- "Pushbutton sprays" employ fluorocarbons as propellants
- Nitrogen-fluorine compounds, such as NF_3, which promise important military and commercial applications

4.27. Preparation of the Halogens

The members of the halogen family are prepared in essentially the same manner because of the similarity of their properties. The more stable halides require greater energy to liberate them from their compounds.

One general method of preparation involves reacting the halide with manganese dioxide and sulfuric acid. The general equation for this reaction is:

$$2Na(\textit{Halide}) + 2H_2SO_4 + MnO_2 \rightarrow Na_2SO_4 + MnSO_4 + 2H_2O + (\textit{Halogen})_2$$

CAUTION: Use hood for all halogen preparations.

a. Chlorine. *Note:* Chlorine can be collected over water conveniently, when large quantities are needed, due to its slow rate of solution.

(1) React HCl (1:1) and $KMnO_4$ (see upper diagram 4.27*a*). Add the HCl drop by drop. The equation for the reaction is:

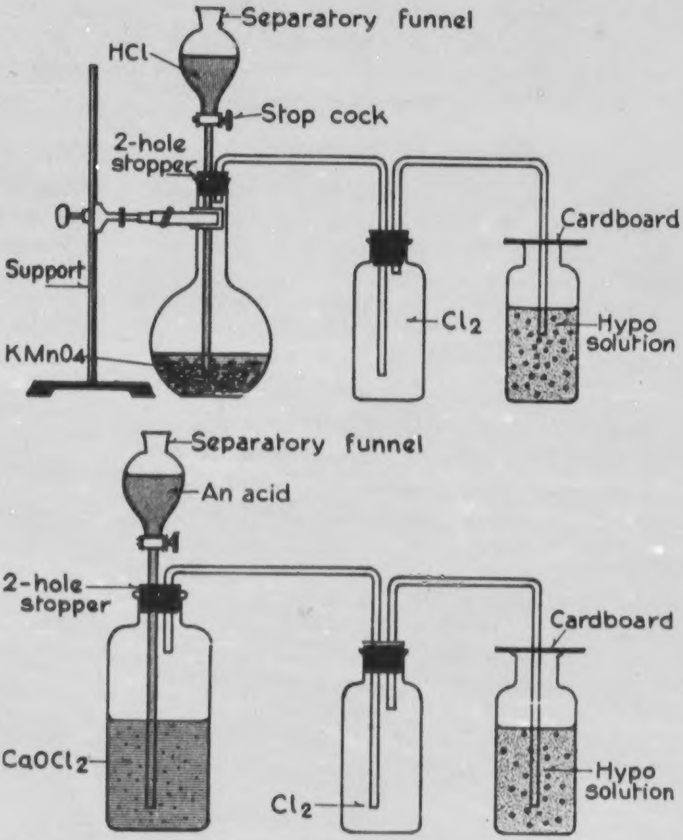
$$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

(2) Treat NaCl with sulfuric acid (1:4) and an oxidizing agent such as manganese dioxide. The apparatus used is the same as shown in (*1*) above.

(3) A convenient method to prepare chlorine is to add an acid to bleaching powder (calcium hypochlorite). Various acids may be used. Chlorine is the product in all cases (see lower diagram 4.27*a*).

(4) The electrolysis of concentrated hydrochloric acid will produce equal volumes of hydrogen and chlorine. Use the electrolysis of water apparatus with graphite electrodes.

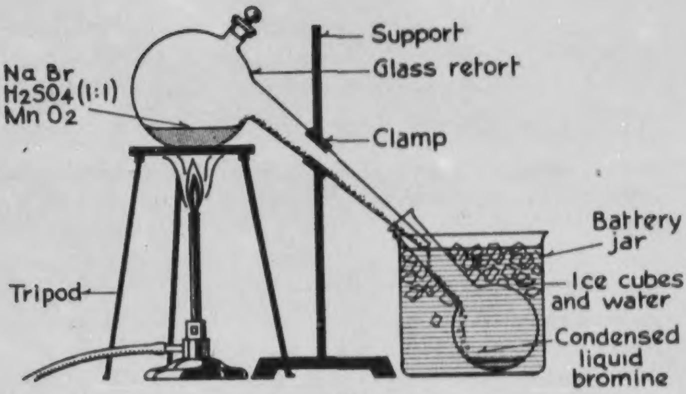
b. Bromine. *CAUTION: Bromine is very corrosive and harmful to skin tissue, particularly the eyes. Do not breathe bromine vapor or allow it to come in contact with the skin. Keep dilute ammonia solution nearby in case of spills.* Bromine may be prepared similarly to chlorine by oxidation from a binary acid (HBr). However, a more convenient method is to start with a bromide (KBr or NaBr), sulfuric acid (1:1) and an oxidizing agent such as manganese dioxide. A glass retort is used in the preparation of bromine. Bromine may be collected under water since it is only slightly soluble in water or may be condensed directly to the liquid (see diagram 4.27*b*).


Separatory funnel
HCl
Stop cock
2-hole stopper
Cardboard
Support
Cl_2
Hypo solution
$KMnO_4$
Separatory funnel
An acid
2-hole stopper
Cardboard
$CaOCl_2$
Cl_2
Hypo solution

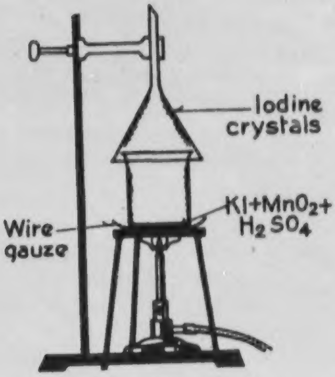
4.27a

Note: Pupil preparation of bromine should be limited to small quantities. Enough bromine can be made from 1 gm. of potassium bromide for all the necessary tests.

c. Iodine. *CAUTION: Avoid handling the iodine crystals or breathing the vapor.* Place 2 gm. of potassium iodide or sodium iodide in a beaker. Add an equal volume of manganese dioxide (about 4 gm.) and mix thoroughly. Now add 5 to 10 ml. of sulfuric acid (1:1) and heat gently. The iodine formed will crystallize on the cool surface of the funnel as shown in diagram 4.27*c*. Remove the funnel and examine the crystals.


Na Br
H_2SO_4(1:1)
Mn O_2
Support
Glass retort
Clamp
Tripod
Battery jar
Ice cubes and water
Condensed liquid bromine

4.27 b


Iodine crystals
KI+MnO_2+ H_2SO_4
Wire gauze

4.27c

4.28. Some Properties of Chlorine

a. Sprinkle powdered antimony into a jar of chlorine. The antimony will spontaneously ignite.

b. Heat each of the following and thrust them into separate jars of chlorine: aluminum, zinc, steel wool and copper foil.

c. Place a short candle on a deflagrating spoon. Light it and insert into a bottle of chlorine.

d. Dip a piece of filter paper into some warm turpentine. Using a forceps, insert the moist filter paper into a bottle of chlorine.

e. Add about 50 ml. of water to a bottle of chlorine and shake the mixture. Add a piece of colored cotton cloth or a red carnation. *Note:* Not all dyes will bleach in chlorine water. Repeat, using a bottle of dry chlorine.

f. TEACHER DEMONSTRATION ONLY: Ignite some red phosphorus on a deflagrating spoon and lower the burning phosphorus into a bottle of chlorine. Repeat, using burning sulfur in place of the phosphorus. Repeat again, using a glowing piece of charcoal.

4.29. Some Properties of Bromine

a. Demonstrate the formation of hydrogen bromide by bubbling hydrogen through liquid bromine. Use an outlet tube made of a piece of glass drawn to a smaller diameter at one end. Ignite the hydrogen and bromine mixture as it emerges from the tip. Test for evidence of hydrogen bromide with moist litmus paper and by blowing breath across the tip to show fuming action (similar to HCl with water vapor).

b. Sprinkle some powdered antimony into a test tube containing both bromine vapor and some bromine liquid at the bottom. Spontaneous combustion will occur.

4.30. Some Properties of Iodine

a. The following is a particularly effective method of demonstrating the sublimation of iodine. Heat 10 gm. of iodine in a 1-liter Florence flask fitted with a one-hole rubber stopper through which is placed a glass tubing about one meter long. The vapor of iodine can be seen ascending the tube and will sublime on the side walls with no vapor escaping from the top. Crystals can be removed with a thin glass rod. Ask pupils to check a handbook and compare subliming temperatures and melting temperatures.

b. Iodine reacts with metals to form salts. Mix powdered zinc with iodine in an evaporating dish. Add several drops of water with a medicine dropper. An immediate combination will occur. Powdered aluminum may be used in place of zinc.

c. Demonstrate the formation of the blue color of iodine with a starch solution. Add a few drops of chlorine water or pass hydrogen sulfide through the solution. The blue color disappears.

4.31. Relative Activity of the Halogens

Discuss the activity of the elements in Group VII*A* on the basis of: (1) increasing molecular weights, (2) electronic structure and (3) ionic radii.

Element	Ionic Radii Å
Fluorine	1.36
Chlorine	1.81
Bromine	1.95
Iodine	2.16
Astatine	2.22

See also activities 2.20 and 2.21.

a. Place 100 ml. of 10 percent solution of potassium bromide in the bottom of a 1-liter cylinder. Conduct chlorine gas from a tank or generator to the bottom of the cylinder through a piece of long glass tubing and bubble the gas through the solution slowly. After a while bromine vapor will be evident above the liquid. This is similar to the method of obtaining the element from sea water.

b. To show that bromine is more active than iodine, add bromine water to a solution of potassium iodide in a test tube to which several milliliters of CS_2, CCl_4 or $CHCl_3$ have been added and shake. The replaced iodine will produce a violet color in the organic solvent. Repeat, using only bromine and an organic solvent to show the color produced.

4.32. Identification of Bromine and Iodine

a. To test for the bromide ion, add chlorine water or several milliliters of potassium permanganate solution and 5 ml. of carbon tetrachloride to the solution and shake. Free bromine is extracted into the carbon tetrachloride layer producing a brownish red color.

b. To test for iodide ion, add chlorine water (or bromine water) and 5 ml. of $CHCl_3$, CCl_4 or CS_2. The free iodine is extracted into the solvent layer, producing a violet shade. The color obtained will vary with the solvent used.

c. To test for free iodine add potassium iodide solution to dilute starch solution. No color change occurs. Add a dilute solution of iodine to starch and blue color is obtained. Iodine dissolved in potassium iodide will similarly produce the blue color. *Note:* If chlorine water is used to liberate free iodine, an excess of chlorine will cause the blue color to disappear.

d. To show the effect of iodine and starch solution dissolve some potassium iodide in a starch solution. Writing made with this solution on paper is almost invisible. Develop the writing by moistening the paper with hydrogen peroxide. To eradicate the writing, use either sodium hypochlorite or oxalic acid.

4.33. Some Uses of the Halogens

a. Chlorine. The United States productive capacity for chlorine amounts to more than 11,000 tons per day. Production of paper consumes the largest portion, about 15 percent. Solvents, automotive fluids, including tetraethyl lead, and plastics each require more than 10 percent of the supply (see reference *4R-26)*. Some newer uses include treatment of industrial wastes, halogen-quenched geiger tubes and rocket propellants (as ammonium perchlorate).

b. Bromine. There are relatively few uses of plain bromine. Two important uses are:

- The production of gasoline additives, such as ethylene bromide
- Testing for unsaturation in organic compounds

c. Iodine. Iodine is a specific necessity in the diet for synthesis of the thyroid hormone. It has uses in the production of germicides and photographic compounds and in analytical reactions (iodimetry). A recent development is its use in purifying metals such as zirconium by causing the vaporized iodide compound of the metal to decompose on a heated filament, depositing the metal. A repeating iodine cycle has been successfully applied to tungsten lamps. Traces of iodine gas in the bulb react with the tungsten which evaporates from the lamp's filament. When the tungsten iodide circulates back to the filament, heat breaks down the compound. Tungsten then deposits on the filament and iodine is free to repeat the cycle. The bulbs are highly efficient but, because the filament must be near the walls, require use of quartz instead of glass for the envelope.

4.34. Properties of Hydrogen Chloride and Hydrochloric Acid

a. Place a piece of dry blue litmus paper in a bottle of dry hydrogen chloride and demonstrate the nonacidic properties of the gas. Now add 25 ml. of water and shake. The litmus turns red. The solution will react now with zinc to produce hydrogen.

b. Over the mouth of a bottle of hydrogen chloride gas invert another bottle containing ammonia gas. Note the formation of the white smoke, NH_4Cl.

c. Blow across the mouth of a bottle containing hydrogen chloride; note the formation of the fumes of hydrochloric acid.

d. Demonstrate the action of an hydrogen chloride fountain. Fill a round bottom 1-liter flask with hydrogen chloride gas. Stopper with a one-hole stopper containing a section of glass tubing, one end drawn to a smaller diameter. Invert the flask over water as shown in diagram 3.19. The water will slowly rise in the tube until a few milliliters of water enter the flask. The hydrogen chloride gas dissolves, forming a partial vacuum. Water rushes into the flask, forming a fountain. A drop of blue litmus in the water increases the effectiveness of the demonstration.

e. Grind together 1 part by weight of sodium chloride and 2 parts of dry $NaHSO_4$ to a fine powder. Fill two 8-inch x 1-inch test tubes to a depth of 2 inches with the mixture. Form a loose ½-inch plug of asbestos fibers or pyrex glass wool and place 3 inches above the salt mixture. Place a ½-inch layer of fine iron filings (or powder) on the plug in one test tube and of granulated tin on the other. Cover each with a second plug of asbestos or glass wool. Heat the metal red hot with a burner flame and heat the salt mixtures with a second burner to generate hydrogen chloride gas. Observe the metal for an indication of reaction. Cool the apparatus at the conclusion of the reaction. The products may be tested as follows: Shake the product from the tube in which iron was placed in a test tube of water and add dilute sodium hydroxide solution. A green gelatinous precipitate is characteristic of iron (II) hydroxide. Prepare a similar solution from the product derived from the tin. When treated with Hg_2Cl_2 it turns gray as it is reduced to free mercury. This behavior is characteristic of tin (II) salts.

Hydrogen chloride produces the metallic chlorides of lower oxidation states of the metals in contrast to the action of chlorine which produces iron (III) and tin (IV) chlorides.

4.35. Etching Glass with Hydrofluoric Acid

TEACHER DEMONSTRATION ONLY: CAUTION: Hydrogen fluoride is an extremely hazardous liquid and vapor which causes severe burns that may not be immediately painful or visible. Immediately flush exposed skin under water until the whiteness disappears. Pay particular attention to skin under nails. Refer the burned person to his physician. Handle the wax bottle of the acid carefully so that the fingers do not accidentally penetrate the wax. Wear rubber gloves and work under the hood. A more interesting procedure than the usual exercise on glass etching is described as follows: Melt some paraffin in a dish and brush this hot material onto one side of a piece of glass. Several pieces may be prepared at the same time. When the paraffin has cooled, hold the glass over the flame, paraffin side down. As the paraffin melts, allow the excess to drain back into the dish. In this way a uniform and very thin coating is obtained. Obtain a child's drawing book of line drawings. Lay the glass, wax side up, over a drawing that you wish to reproduce. Use a sharp lead pencil to trace the lines of the drawing, cutting down into the glass. Brush away any loosened wax. Now brush hydrofluoric acid into the tracings. Allow the acid to remain in contact until the next day. Rinse off the acid, scrape off the paraffin, rub with carbon tetrachloride and then wash with soap and water. (*Note:* Wax may be removed from the glass plate by dipping glass plate into hot water, drying it and then rubbing it with carbon tetrachloride.) Rub over the etching with aluminum paint that has been thinned with turpentine and wipe off with a clean cloth. The lines of the etching will appear as silver. Other materials such as red enamel and bronze paint may be used.

4.36. Occurrence and Forms of Sulfur

a. Heat some mineral oil in a beaker to 125°C. and insert a test tube containing small lumps of sulfur. The sulfur melts at about 113°C. Relate to the Frasch process of mining sulfur.

Note that some of the largest sulfur deposits have been found offshore in the Gulf of Mexico. Hot pressurized sea water is used as the mining tool, and the molten sulfur is brought to shore as a liquid in insulated barges. The mining rigs themselves can usually be floated to new locations when one site is exhausted.

b. Considerable sulfur occurs as H_2S contaminating natural gas supplies ("sour gas"). Illustrate the method of removal by inverting a jar of moist sulfur dioxide over a jar of moist hydrogen sulfide. The sulfur is precipitated according to the reaction:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O$$

The sulfur is generally used to produce sulfuric acid.

c. To prepare rhombic crystals, dissolve 1 gm. of sulfur in 2 ml. of CS_2 and pour onto a watchglass. Place on the overhead projector. Within a few minutes rhombic crystals will form. For larger crystals, saturate 20 ml. of CS_2 with sulfur and filter carefully into a petri dish. Cover with several layers of filter paper held down by a book to retard evaporation of the solvent. In a few days, large crystals will form. For crystals of spectacular size, see reference *4R-27*.

d. Heat sulfur in a casserole until it is just slightly above its melting point. Pour half the contents into a filter paper cone and open up the cone before the sulfur has completely set. Examine the needle-shaped crystals of monoclinic sulfur. On standing, the crystals slowly revert to the rhombic structure, although the appearance of needles will remain.

e. Continue to heat the balance of the sulfur from *d* above until dark and free flowing, then pour slowly from a height into a large beaker of cold water. When cool, pass the elastic strands of plastic sulfur to the pupils for examination.

4.37. Properties and Uses of Sulfur

a. Mix well equal parts of ground sulfur and iron filings and pour the mixture into a test tube. Heat the test tube until the sulfur-iron mixture begins to glow of its own accord. Cool, break the test tube, and examine the contents. Test with a magnet for the presence of iron. Test the solubility of the contents in CS_2. Add HCl to test for a sulfide.

b. Heat a test tube that is about one-third full of sulfur until the sulfur is boiling and insert a strip of copper foil. Note the change in the copper. Add HCl and test for evidence of H_2S.

c. TEACHER DEMONSTRATION ONLY: Grind 2 gm. of powdered sulfur with several drops of mercury in a mortar. A direct combination of sulfur and mercury occurs.

d. TEACHER DEMONSTRATION ONLY: Mix well 1 gm. of powdered zinc and 2 gm. of powdered sulfur. Place this mixture in the form of a cone on an asbestos pad that rests on a tripod. Place in the hood. Ignite the mixture with the flame of a bunsen burner held at arm's length. *CAUTION: A violent reaction occurs with the formation of ZnS.* Test the solid formed with HCl for evidence that a sulfide is formed.

e. Place a piece of sulfur the size of a pea in a deflagrating spoon. Place in the hood and ignite in the bunsen flame. Insert into a bottle containing chlorine gas. The combustion will continue with the formation of a mixture of the chlorides of sulfur. A highly disagreeable odor will be evident.

f. Demonstrate the solubility of sulfur. Into separate test tubes, place samples of the three forms of sulfur prepared in activity 4.36. Add 10 to 20 ml. of CS_2 to each and shake each test tube. Pour the contents of the test tubes on individual watchglasses and allow the liquid to evaporate. Examine the residue and compare the solubilities of the three forms. *CAUTION: CS_2 gives off poisonous, flammable and explosive vapor. Use an exhaust hood and keep it away from an open flame.*

g. Discuss the uses of sulfur including some of the following points:

- Sulfur consumption in the United States historically has paralleled the advance in general industrial activity. Present per capita consumption is about 75 pounds per year.

- About 80 percent of our sulfur production goes into sulfuric acid. One-third to one-half of the sulfuric acid produced goes into the manufacture of fertilizers.
- About 35 pounds of sulfur are needed to make one automobile.
- Synthetic rubbers and plastics containing sulfur ("thiokols") are finding many uses, from weather-proofing the United Nations building to solid propellants for rockets.
- A frontier of sulfur chemistry is represented by the development of low-melting glasses, containing sulfur, arsenic and thallium.

4.38. Preparation of Sulfur Dioxide

a. Ignite a piece of sulfur on a deflagrating spoon and lower it into a widemouthed bottle containing oxygen. The sharp distinctive odor of SO_2 is evident. Add 25 ml. of H_2O and shake the bottle. Test the solution with litmus to show the formation of H_2SO_3.

b. Pour some concentrated HCl on sodium sulfite or sodium bisulfite in a flask fitted with a thistle tube and delivery tube as shown in diagram 4.38*b*. Collect the SO_2 formed by upward air displacement since it is both soluble in water and heavier than air. *CAUTION: SO_2 is a poisonous gas and very irritating to the mucous membranes. Permit a minimum of gas to escape into the room.* Pour the sulfur dioxide solution onto a flat plate in the hood or on a window sill; the odor disappears rapidly.

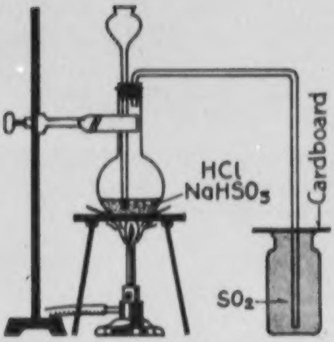
4.39. Properties and Uses of Sulfur Dioxide and Sulfurous Acid

a. **Ease of Liquefaction.** Sulfur dioxide may be easily liquefied (see diagram 4.39*a*).

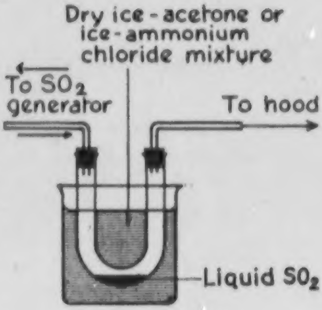
b. **As a Bleaching Agent.** To a bottle or jar containing SO_2, add a pink carnation, red rose or some fuchsin dye solution. The color will slowly fade out. The color may be restored by using an oxidizing agent such as H_2O_2 or dilute nitric acid.

c. **As a Reducing Agent.** Pass SO_2 through an acidified solution of $KMnO_4$. The color quickly fades due to formation of Mn^{++++}. Either HCl or H_2SO_4 may be used to acidify the $KMnO_4$. Repeat, using potassium dichromate; it turns green due to formation of Cr^{+++}.

d. **As Both an Oxidizing and Reducing Agent.** Form H_2SO_3 by dissolving SO_2 in water. Test with litmus to show its acidic property. Test with barium chloride to show the presence of sulfite ions soluble



4.38b



4.39a

in HCl (see activity 4.40). Now expose the solution of sulfurous acid to an ultraviolet light source. The acid gradually undergoes auto oxidation-reduction and sulfur is precipitated as milk of sulfur. Test with barium chloride for evidence of the sulfate ion.

e. **As a Nonsupporter of Combustion.** Insert a burning splint into a bottle of SO_2. The splint goes out. However, in certain catalytic oxidations, SO_2 is actually used as the source of oxygen.

f. **Solubility.** Fill a large dry graduate with SO_2. Invert into a basin of water and allow to stand. In about 30 minutes the graduate is filled with water. Test with a large piece of litmus paper to show the presence of H_2SO_3.

g. **Sulfurous Acid as an Oxidizing Agent.** Sulfurous acid usually acts as a reducing agent by extracting oxygen from other substances and becoming oxidized to a sulfate. It can, however, be used to bring about oxidation.

Add sulfurous acid to hydrogen sulfide solution. Sulfur precipitates, as follows:

$$H_2SO_3 + 2H_2S \rightarrow 3H_2O + 3S$$

The sulfur of sulfurous acid changes in valence ($S^{++++} + 4e \rightarrow S^0$). This is a reduction. The valence of the sulfur of hydrogen sulfide also changes from —2 to 0 ($S^{--} - 2e \rightarrow S^0$). This is an oxidation.

4.40. Test for the Sulfite Ion

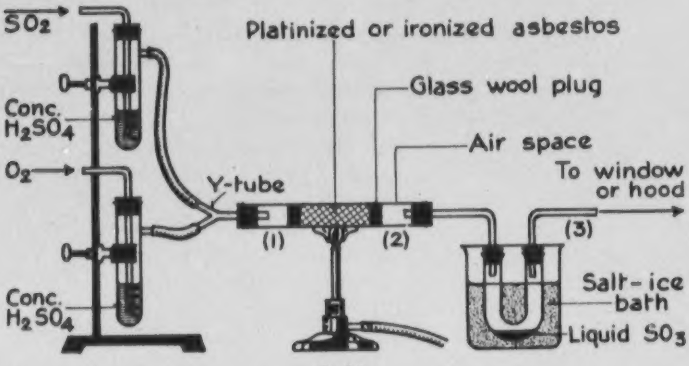
To test for the presence of the sulfite ion, add a solution of barium chloride. Add concentrated hydrochloric acid to the white precipitate. Note the solubility. A confirmatory test involves the reduction of potassium permanganate to the colorless state. Add a solution of

$KMnO_4$ acidified with a few drops of concentrated HCl to the sulfite. Note the color change.

4.41. Preparation of Sulfuric Acid

At least the crucial part of the contact process should be demonstrated, as in diagram 4.41. *Note:* Add supports at points *1*, *2* and *3*. Use a tank source of SO_2 and O_2 for convenience and pass the gases at a rate of one bubble a second. When the catalyst reaches proper temperature, white clouds of SO_3 will appear. When the temperature goes too high, its formation will cease. Remove the bunsen burner and allow the tube to cool until the correct temperature range is again entered. Wire the stoppers on the bubble counters so that a sudden surge of gas cannot force them out with danger of splashing the acid about.

Ironized asbestos is prepared by soaking Gooch (filtering) asbestos with 10 percent ferric chloride solution, then adding concentrated ammonia to precipitate the hydroxide. Filter, wash and dry well in an oven at 150°C. Sulfur trioxide is not very soluble in water, but enough will dissolve to give a test for sulfate ion. Contrast with its solubility in H_2SO_4.



4.41

4.42. Properties and Uses of Sulfuric Acid

a. As an Oily, Heavy Liquid. Pour some concentrated acid from one beaker to another to display its physical properties. Compare the weight of the acid with that of an equal volume of water. *CAUTION: Never permit pupils to handle concentrated sulfuric acid, except in small amounts.*

b. As a Dehydrating Agent.

(1) To a 250-ml. beaker half full of cane sugar, add 100 ml. of concentrated H_2SO_4. Within a few seconds the sugar will begin to char with the escape of steam and the reduction products of H_2SO_4. A great deal of heat is evolved. *CAUTION: Do not let pupils handle the charred carbon, until it has been thoroughly washed to remove all traces of acid.*

(2) Repeat, using different forms of cellulose. Dip into separate test tubes of H_2SO_4: a wood splint, a roll of paper and cotton cloth. *CAUTION: Do not allow pupils to handle the charred carbon.*

c. As an Oxidizing Agent.

(1) Place several pieces of mossy zinc in a large test tube. Add concentrated H_2SO_4 and heat gently. Note the evolution of both H_2S and SO_2. Demonstrate the presence of H_2S with moist lead acetate paper. Repeat with zinc and dilute H_2SO_4 and demonstrate that now hydrogen gas is evolved. Impurities in zinc exercise a catalytic effect on this reaction. Zinc purified by electrolysis produces appreciable H_2, even with concentrated acid.

(2) Sulfur dioxide can be prepared conveniently by heating any form of copper metal in a flask containing concentrated H_2SO_4. Anhydrous copper sulfate is a byproduct.

d. As an Acid.

(1) Demonstrate the difference in conductivity between dilute and concentrated acid. Use an unfrosted lamp bulb in the standard conductivity testing apparatus. Most commercial acids contain too much water to show this effect. Try fuming sulfuric acid or pass some SO_3 through the concentrated acid before testing.

(2) Recall the use of H_2SO_4 to prepare other acids such as HCl and HNO_3 both as the source of the hydrogen ions and as a high boiling point medium. *CAUTION: Always add sulfuric acid to water. The reverse process will cause the acid to splatter in all directions. When diluting concentrated sulfuric acid, always add the acid slowly to the water with considerable stirring. A wash basin below the receptacle is a good additional precaution. A great deal of heat is involved during solution and even pyrex beakers have been known to shatter.*

e. Uses. Tabulate the more important uses of sulfuric acid. Some of the large nonagricultural uses are: pickling iron and steel, producing inorganic pigments, production of synthetic detergents, purification of petroleum, production of hydrochloric and hydrofluoric acids and sulfate salts for various purposes. Production of phosphate fertilizers is the greatest use. Point out an increasing trend to industrial use of SO_3 shipped in liquid form; one application is the fortification of spent acid for re-use.

4.43. Test for the Sulfate Ion

a. Demonstrate the test for the sulfate ion by adding about 5 ml. of barium chloride solution to a 500-ml. Florence flask that contains about 25 ml. of dilute sulfuric acid in 150 ml. of water. Shake the flask and hold it against a black background to show the formation of white barium sulfate. Add 15 ml. of concentrated HCl to show the insolubility of $BaSO_4$ in acid solution.

b. Based on the reaction in *a* ask the class to design an apparatus for detection of sulfuric acid in polluted air.

c. Demonstrate the atmospheric oxidation of sulfur dioxide. Prepare fresh sulfurous acid by passing SO_2 through cold water. Show that no sulfate ions are present by testing a portion of the liquid for the sulfate ion. Allow to stand in an open beaker overnight and test again the next day. The oxidation can be accelerated by adding hydrogen peroxide.

4.44. Preparation of Hydrogen Sulfide

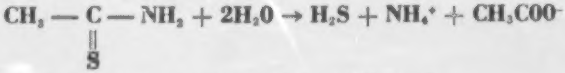
a. Hydrogen sulfide is prepared in the laboratory by the general method of adding an acid to a sulfide. The use of a thistle tube facilitates the addition of acid. Where large quantities of H_2S are required, a Kipp generator is suggested. *CAUTION: Gaseous H_2S is a dangerous poison because of its paralyzing action on the respiratory nerve centers. Exposure to the gas may produce headaches, nausea and fainting. All laboratory work involving the use of H_2S should be done under a hood or with a good exhaust fan operating in the room. No pupil should work alone with H_2S.*

Set up the apparatus as shown in a conventional diagram. Hydrochloric acid is added to iron (II) sulfide to produce H_2S. Copper sulfate or potassium permanganate solutions may be used to prevent the escape of hydrogen sulfide into the room.

b. Laboratory quantities of H_2S may be prepared by heating a mixture of sulfur, paraffin and shredded medium-grade asbestos. The evolution of the gas is controlled by the heating. Place a mixture of 20 gm. of powdered sulfur, 5 to 10 gm. of chopped paraffin and an equal volume of shredded asbestos in a large pyrex tube. Insert a one-hole stopper and delivery tube. Heat the test tube to produce H_2S as needed. The tube can be stored and reused. Rosin may be substituted for the paraffin with similar effects.

c. The use of thioacetamide is rapidly replacing H_2S gas in all versions of analytical chemistry. Its use in the high school is *highly recommended.* While relatively expensive, it is used in a stable 5 percent aqueous solution and only small amounts are required. In use, the solution is added to the material to be tested and warmed to 80°C. or above. A beaker of boiling water makes a useful bath for this step if the reactions are performed in test tubes. At this temperature the normally stable thioacetamide hydrolyzes appreciably as follows:

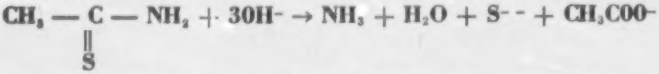
Neutral or acid solutions:



$$CH_3 - \underset{\underset{S}{\|}}{C} - NH_2 + 2H_2O \rightarrow H_2S + NH_4^+ + CH_3COO^-$$

The H_2S hydrolyzes as follows: $H_2S \rightleftarrows 2H^+ + S^{--}$

In basic solutions:



$$CH_3 - \underset{\underset{S}{\|}}{C} - NH_2 + 3OH^- \rightarrow NH_3 + H_2O + S^{--} + CH_3COO^-$$

The sulfide ion reacts immediately with the cation, and little or no odor is apparent.

4.45. Properties and Uses of Hydrogen Sulfide

a. Show that H_2S is a reducing agent, and therefore oxidizable. Pass the gas through test tubes containing dilute nitric acid, concentrated nitric acid, 3 percent hydrogen peroxide and acidified $KMnO_4$ solution. Oxidation to sulfur, sulfite or sulfate may occur; test with barium chloride. See M.C.A. experiment *No. 23.*

b. Invert a test tube of dry H_2S into a dish of water and allow to stand. The water rises slowly indicating solubility. This process is slow enough to permit the collection of H_2S by displacement of water if this is considered convenient.

c. Burn a test tube of pure H_2S. The burning rate is slow and sulfur forms. Mix one part of H_2S with seven parts of air and ignite. Rapid burning results with production of sulfur dioxide.

d. Illustrate the use of H_2S in analytical chemistry by adding the gas or a fresh aqueous solution of H_2S to test tubes containing ions of zinc, cadmium, lead, antimony, copper, arsenic, silver and an "unknown" (see page 336 for sulfide precipitates). See also activity 4.44*c*.

e. Clean several pieces of silverware or coins, then expose to H_2S in order to tarnish them. Line a beaker with aluminum foil, then add water and a tablespoonful of baking soda. Heat the water and add the tarnished silverware. Exhibit the clean silver to the class. Air commonly contains traces of H_2S from decaying proteins and tarnish occurs when the gas is oxidized to sulfur, perhaps with a catalytic effect from the metallic surface. The sulfur then reacts with the silver.

4.46. Test for the Sulfide Ion

a. To test for the presence of the sulfide ion, add an acid (HCl) to the unknown and test any gas evolved with moist lead acetate paper. A silvery-black color is evidence for H_2S. Lead acetate paper is prepared by dipping a piece of filter or blotter paper into a solution of lead acetate. Any soluble lead salt may be used with similar results.

b. Silver nitrate may be used to test for the sulfide ion. To a solution of the unknown, add several milliliters of silver nitrate. Ag_2S, a black precipitate insoluble in HNO_3, will form if the sulfide ion is present.

4.47. Occurrence of Nitrogen

a. Besides the atmosphere and the biosphere, a vast reservoir of nitrogen exists in the lithosphere. Volcanic gases have long been known to contain nitrogen. Silicate minerals seem to hold the nitrogen trapped in pockets in their lattice structure as ammonium ions (and other forms). One estimate places the lithosphere as 20 times richer in nitrogen than the earth's atmosphere. The earth's atmosphere is believed to have contained large amounts of ammonia when the earth's surface was still hot (see reference *4R-28).*

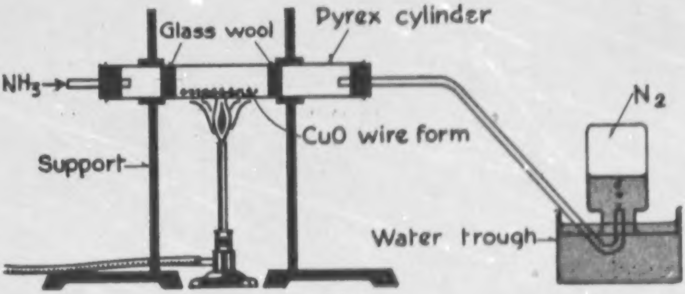
b. TEACHER DEMONSTRATION ONLY: While rather inert, the nitrogen of the atmosphere does react during high temperature combustions. Place a 1-inch cone of magnesium turnings *(not powder)* on an asbestos pad and ignite the top of the cone with a bunsen burner. Direct a stream of nitrogen from a tank of the gas over the hot metal. Show that traces of yellow magnesium nitride, Mg_3N_2, are present. Dump the cold residue into water to form magnesium oxide and ammonia and perform a test for ammonia with a copper sulfate solution.

c. Point out that atomic nitrogen is very reactive, as exhibited in the atomic nitrogen torch. The nitrogen in the atmosphere has been considerably stabilized by the formation of the diatomic molecule with covalent bonds.

4.48. Preparation and Properties of Nitrogen

a. The gas remaining after oxygen is removed from air is approximately 100 percent nitrogen. Float in a pan of water a piece of yellow phosphorus on a cork 2 or 3 inches in diameter. Ignite the phosphorus by means of a heated stirring rod and cover with a bell jar stoppered at the top. Allow time for the phosphorus pentoxide (P_4O_{10}) to dissolve in the water. The water will rise to replace the oxygen removed. Remove the stopper from the top of bell jar and test the gas remaining with a burning splint. The flame will be extinguished immediately. A lighted candle may be used instead of the phosphorus. Use limewater in the pan to absorb the carbon dioxide. The limewater need not be filtered.

b. Nitrogen may be prepared in the laboratory by passing ammonia from any convenient source over hot copper (II) oxide (wire form). The nitrogen is collected by water displacement. Any ammonia passing through the tube dissolves in the water. *CAUTION: Remove the delivery tube from the trough before removing heat.* The apparatus is illustrated in diagram 4.48*b*.

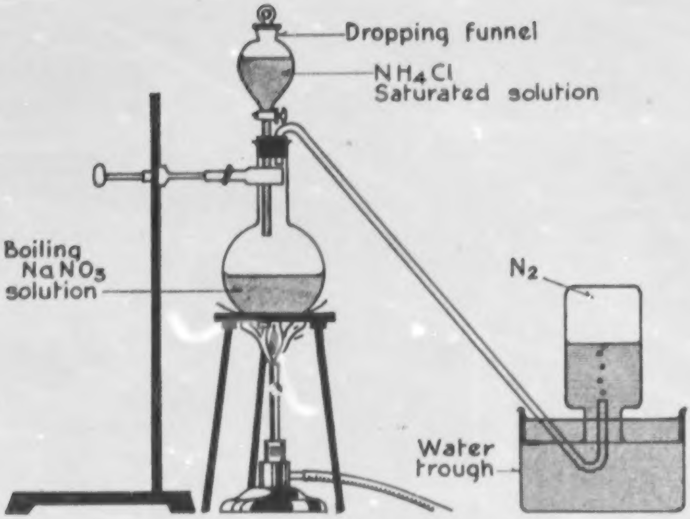


4.48b

c. Nitrogen may be prepared by the decomposition of a nitrate. The direct heating of a nitrite may be dangerous and the following procedure is suggested. Arrange a dropping funnel containing a saturated solution of ammonium chloride so that it may be added drop by drop to a sodium nitrate solution (25 gm. per 100 ml.) in a flask which is kept almost at the boiling temperature. Nitrogen is collected by water displacement. *CAUTION: Remove the delivery tube from the trough before removing the heat.* See diagram 4.48*c* for the apparatus used.

d. CAUTION: Under no circumstances should nitrogen tri-iodide experiments be performed in the high schools. As a substitute for a demonstration, discuss the instability of many nitrogen compounds.

e. Some compounds of nitrogen are very stable. An example is boron nitride, a white solid similar in slipperyness, density and crystal structure to graphite (hexagonal). Under heat and great pressure it can be converted to a cubic crystal structure, like diamond. This substance, cubic boron nitride ("borazon"), scratches a diamond with ease, the only material known to be able to do this, besides other diamonds.



4.48C

Moreover, it can withstand temperatures up to 3,000°F. and has good resistance to oxidation. Its use as a substitute for industrial diamonds is under consideration.

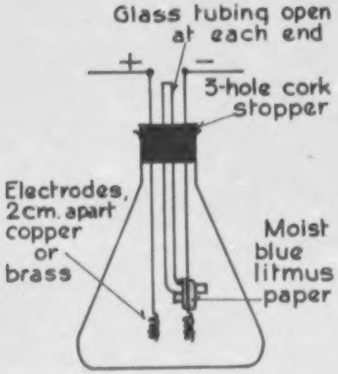
4.49. Nitrogen Fixation

a. To demonstrate the direct combination of nitrogen and oxygen by electrical discharge (arc process) use the apparatus shown in diagram 4.49*a*. Use any good induction coil to produce the spark. The arc between the two copper wires (2 cm. apart) causes the direct union of the nitrogen and oxygen of the air. The nitric oxide formed is converted by the oxygen in the air to the brown nitrogen dioxide fumes which are visible. For greater visibility, place a white card behind the flask.

Bend a piece of glass tubing to support a piece of moist blue litmus paper. Leave the ends of the tubing open for the entry of the air. The moistened blue litmus paper turns pink in 10 to 20 minutes which shows the formation of an acid.

Disconnect the leads, add 10 ml. of cold water, stopper and shake well. Pour out the solution and perform the brown ring test for nitrates. See activity 4.53.

The arc process is feasible only where the use of electricity is


Glass tubing open at each end
+
−
3-hole cork stopper
Electrodes, 2cm. apart copper or brass
Moist blue litmus paper

4.49a

economical compared to alternate methods. The slowness of this reaction points out the relative inertness of nitrogen. Lightning produces natural fertilizer in this way. One estimate of the amount produced is 50,000 tons per day, carried down to earth as weak nitric acid in rainfall.

b. The recoil energy of fission particles in nuclear reactors may be commercially developed into a technique for fixing nitrogen (see reference *4R-29*).

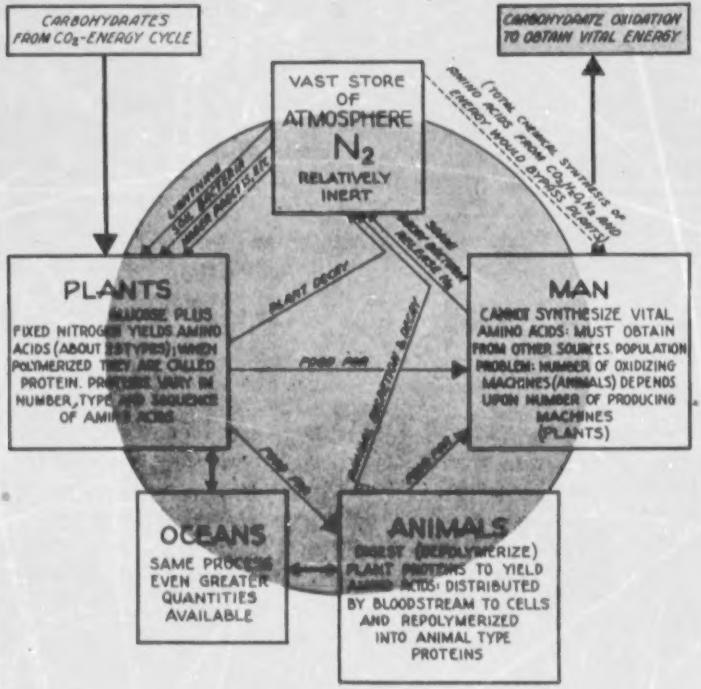
4.50. The Nitrogen Cycle

a. The nitrogen cycle provides an opportunity to organize the relationships among many chemical reactions (see diagram 4.50*a*).

b. The problem of world food supply is largely a problem in chemistry. Approaches to the problem involve:

- Synthetic production of fertilizers, most of which are made from ammonia manufactured by the Haber process
- Soil conditioners and films to retard the evaporation of water
- Marine agriculture of fish and plant life
- Producing more food per arable acre with balanced fertilization, weed control and insect control
- Acceleration of plant growth by gibberellic acid or other chemicals
- Development of better methods of preservation of food during transportation and storage
- Possible synthetic imitation of the photosynthesis process.

THE NITROGEN CYCLE


CARBOHYDRATES FROM CO_2-ENERGY CYCLE
CARBOHYDRATE OXIDATION TO OBTAIN VITAL ENERGY
VAST STORE OF ATMOSPHERE N_2 RELATIVELY INERT
(TOTAL CHEMICAL SYNTHESIS OF AMINO ACIDS FROM CO_2, H_2O, N_2 AND ENERGY WOULD BYPASS PLANTS)
LIGHTNING
SOIL BACTERIA
[illegible] ETC.
SOME BACTERIA RELEASE N_2
PLANT DECAY
PLANTS
GLUCOSE PLUS FIXED NITROGEN YIELDS AMINO ACIDS (ABOUT 23 TYPES); WHEN POLYMERIZED THEY ARE CALLED PROTEIN. PROTEINS VARY IN NUMBER, TYPE AND SEQUENCE OF AMINO ACIDS
FOOD FOR
MAN
CANNOT SYNTHESIZE VITAL AMINO ACIDS: MUST OBTAIN FROM OTHER SOURCES. POPULATION PROBLEM: NUMBER OF OXIDIZING MACHINES (ANIMALS) DEPENDS UPON NUMBER OF PRODUCING MACHINES (PLANTS)
ANIMAL EXCRETION & DECAY
FOOD FOR
FOOD FOR
OCEANS
SAME PROCESS EVEN GREATER QUANTITIES AVAILABLE
ANIMALS
DIGEST (DEPOLYMERIZE) PLANT PROTEINS TO YIELD AMINO ACIDS: DISTRIBUTED BY BLOODSTREAM TO CELLS AND REPOLYMERIZED INTO ANIMAL TYPE PROTEINS

4.50a

4.51. Preparation of Nitric Acid

CAUTION: Preparation of nitric acid by direct oxidation of ammonia SHOULD NOT BE ATTEMPTED due to the possibility of explosion of the ammonia-oxygen mixture. Several accidents have resulted from this demonstration.

Nitric acid may be prepared by the addition of sulfuric acid to a nitrate using the conventional all-glass retort apparatus. *CAUTION: Utmost care should be used throughout this exercise since both concentrated sulfuric acid and nitric acid, especially when hot, will cause serious injury to the skin and clothing.*

4.52. Properties of Nitric Acid

a. Impurities in Nitric Acid. Exhibit samples of fresh, clear nitric acid and the yellow acid that forms from exposure to light. The yellow color results from an internal redox reaction and is due to dissolved nitrogen dioxide. Using caution, boil a small sample of the yellow variety in a test tube to show that the color disappears as this gas is expelled.

b. "Fuming Nitric" Acid as an Oxidizing Agent. *TEACHER DEMONSTRATION ONLY:* "Fuming nitric acid" contains dissolved nitrogen dioxide in considerable amounts and is a very powerful oxidizing agent.

(1) Place a piece of glass wool in a petri dish or similar dish. Pour about 5 ml. of fuming nitric acid on the wool. Place the tip of a delivery tube from a hydrogen sulfide generator under the glass wool. A vigorous oxidation (fire) takes place as the hydrogen sulfide comes in contact with the acid.

(2) Place glass wool in a 150-ml. beaker to a depth of 2 to 3 inches. Pour 5 ml. of *warm* turpentine on the wool. Now drop 2 ml. of yellow fuming nitric acid on it by means of a pipette. After a few seconds the turpentine will burst into flames. Glass wool is used to provide a large surface area and because it is inert.

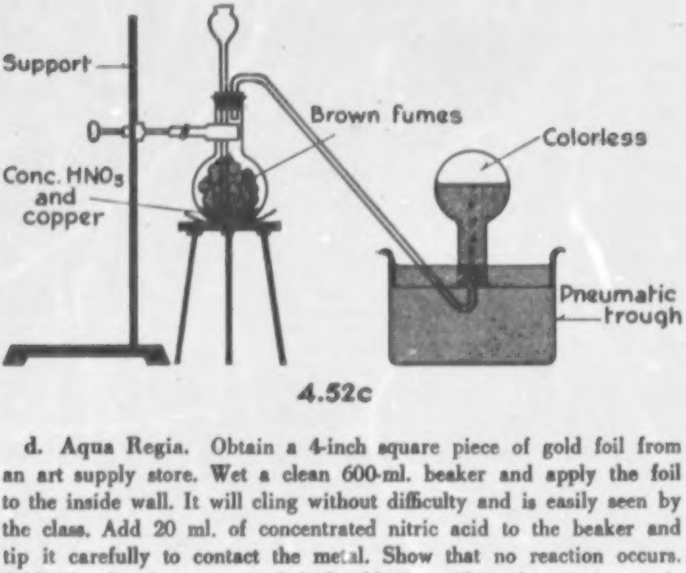
(3) Place about 5 ml. of fuming nitric acid in a pyrex test tube. Loosely insert a plug of straw or excelsior into the mouth of the tube. Heat gently. After a few seconds the straw will suddenly burst into flame. Wool or glowing charcoal may be used in place of excelsior.

c. Concentrated Nitric Acid as an Oxidizing Agent. Concentrated nitric acid used in the laboratory contains 68 percent of HNO_3 by weight. It is a powerful oxidizing agent but not so powerful as "fuming nitric acid." Concentrated HNO_3 will oxidize both nonmetals and metals.

(1) Place 1 gm. of sulfur in a pyrex test tube, cover with concentrated nitric acid and heat to boiling. Cool the mixture and test for the sulfate ion.

(2) Prepare a flask containing copper scraps as in diagram 4.52*c*. Add sufficient concentrated nitric acid to seal the bottom of the thistle tube. A vigorous evolution of brown fumes of nitrogen dioxide occurs. Show that they dissolve in the water of the trough, and no gas except air will collect.

When dilute HNO_3 is used a different gas (nitric oxide) is formed. To the flask above add cold water through the thistle tube to equal or exceed the original quantity of acid. The brown fumes cease and are replaced by a quiet evolution of colorless nitric oxide. (Heat gently if the reaction is too slow.) Quickly change the collecting flask and show that this colorless gas can be collected by water displacement. When the flask is nearly filled, stopper and remove. Pour the acid in the generator off the copper to stop the reaction. Unstopper the flask of nitric oxide admitting air. The brown fumes indicate atmospheric oxidation to nitrogen dioxide. Restopper, and shake; the brown fumes disappear by reaction with the water. Unstopper again (a slight vacuum will be observed) and repeat the procedure several times. Finally, test the solution for the presence of nitrate and hydrogen ions.



4.52c

d. **Aqua Regia.** Obtain a 4-inch square piece of gold foil from an art supply store. Wet a clean 600-ml. beaker and apply the foil to the inside wall. It will cling without difficulty and is easily seen by the class. Add 20 ml. of concentrated nitric acid to the beaker and tip it carefully to contact the metal. Show that no reaction occurs. Add 60 ml. of concentrated hydrochloric acid to form *aqua regia* and show the metal dissolving. *CAUTION: Do not store aqua regia; it may explode.* Soluble auric acid forms in this reaction ($HAuCl_4$) but the exact mechanism is open to question. If it is due to formation of chlorine, then a gold anode should dissolve during the electrolysis of hydrogen chloride but it does not.

e. **Test for Proteins.** Nitric acid is used to test for certain types of proteins. Place the white portion (albumin) of a hard-boiled egg in a 100-ml. beaker. Pour 10 ml. of concentrated nitric acid on the albumin. After the albumin has turned yellow, rinse and neutralize with concentrated ammonium hydroxide. An orange color is evidence of protein material. Repeat, using other examples of protein materials. Wool is an excellent material to use.

4.53. Test for the Nitrate Ion

a. For a class demonstration, use a very large test tube or cylinder. Add 20 ml. of ferrous sulfate solution (approximately 2 gms. to 100 ml. of water) to the tube. The $FeSO_4$ solution should be freshly prepared or poured through a wad of steel wool in a funnel. The iron metal tends to reduce iron (III) to iron (II). Add an equal volume of a nitrate solution. Cautiously and slowly pour about 5 ml. of concentrated H_2SO_4 through a thistle tube extending to the bottom of the container. Hold against a light background to exhibit the "brown ring" which forms at the junction of the acid and the solutions.

b. Place a few drops of a nitrate solution on a piece of plaster. Dissolve a few crystals of diphenylamine in 10 ml. of concentrated sulfuric acid and pour over the plaster. Blue spots indicate the presence of nitrates. This is the basis of a test to determine whether a person's hands have traces of nitrates, indicating recent firing of a gun.

4.54. Compounds of Nitrogen

a. Exhibit a table such as given below to illustrate the range of valence in nitrogen compounds. The oxidation numbers are assigned by the conventional rules. All the bonds are primarily covalent in character. The equilibrium equations suggest that all oxides of nitrogen are mixtures of various types, and this is basically true.

NAME	FORMULA	NITROGEN OXIDATION NUMBER	STATE	COMMENT
Ammonia	NH_3	−3	Gas	Easily liquefied. In liquid state its properties resemble water more closely than any other substance.
Hydrazine	H_2NNH_2	−2	Liquid	Used in chemical synthesis. Derivatives used as rocket fuels.
Hydroxylamine	NH_2OH	−1	Solid	Used as a laboratory reducing agent.
Nitrogen	N_2	0	Gas	Used to provide an inert atmosphere for certain reactions; for example, the Grignard reaction.

Nitrous Oxide or Nitrogen (I) Oxide	N_2O	+1	Gas	"Laughing gas" does not occur naturally. Because its infra-red spectrum is easy to detect it is used as a leak analyzer for pipes.
Nitric Oxide or Nitrogen (II) Oxide	NO	+2	Toxic gas	$2NO \rightleftharpoons N_2 + O_2$
Nitrogen Trioxide or Nitrogen (III) Oxide	N_2O_3	+3	Unstable	$N_2O_3 \rightleftharpoons NO + NO_2$
Nitrogen Dioxide or Nitrogen (IV) Oxide	NO_2	+4	Toxic gas	$2NO_2 \rightleftharpoons 2NO + O_2$ $N_2O_4 \rightleftharpoons 2NO_2$
Nitrogen Pentoxide or Nitrogen (V) Oxide	N_2O_5	+5	Solid, unstable	$N_2O_5 \rightleftharpoons NO_2 + NO_3$
Nitrogen Trioxide or Nitrogen (VI) Oxide	NO_3	+6	Unstable	

b. TEACHER DEMONSTRATION ONLY: CAUTION: The preparation of nitrous oxide by gently heating ammonium nitrate is not recommended since an explosion may occur if heating is too strong.

c. Nitric oxide can be made from the reaction between copper and dilute nitric acid (see activity 4.52*c)*. Another method: Mix 52 gm. of $FeSO_4 \cdot 7H_2O$ with 25 gm. of $NaNO_2$. Hasten the evolution of nitric oxide (NO) by adding a little water. The reaction may be slowed up by chilling in ice.

d. Fill a U-tube with nitrogen dioxide made from copper and concentrated nitric acid, and stopper both ends. At room temperature the gas is a light brown color due to a mixture of the colorless dimer, N_2O_4, and the dark-colored monomer, NO_2. Place one leg of the U-tube in a beaker of hot water, the other end in a beaker of crushed ice. The color in each leg will indicate the effect of temperature on the equilibrium:

$$N_2O_4 \rightarrow 2NO_2$$

At 35°C. the gas is about 30 percent NO_2. See reference *4R-30.*

4.55. Preparation of Ammonia

a. Mix equal amounts of dry ammonium chloride and dry calcium hydroxide to half fill a pyrex test tube. Place the mixture in a pyrex test tube fitted with a one-hole stopper and a delivery tube pointing up. Heat gently. Collect the gas by downward air displacement as shown in conventional diagrams. One side of the glass cover plates may be coated with vaseline.

b. Have pupils mix a pinch of different ammonium salts and slaked lime in the palms of their hands. The heat of the hands is sufficient to liberate the ammonia which may be detected by its odor.

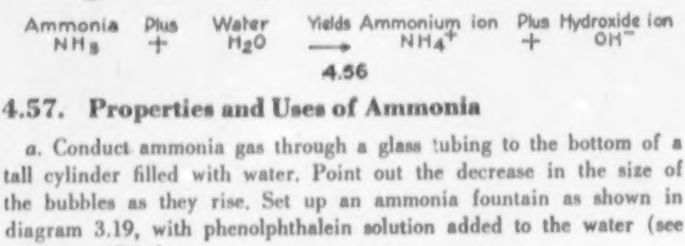
c. Concentrated ammonium hydroxide may be heated to produce ammonia gas. Use a calcium chloride drying tube to dry the ammonia. Moist red litmus paper or tumeric paper may be used to detect the presence of ammonia.

4.56. "Ammonium Hydroxide"

The frequently used term "ammonium hydroxide" and the formula, NH_4OH, do *not* represent a real molecule. It has been proved that no such species exists in aqueous solutions of ammonia.

Some substances which are composed of molecules, such as ammonia, dissolve in water as hydrated molecules and not as hydrated ions. A water molecule is attached to ammonia by a hydrogen bond to form the hydrate: $NH_3\cdots HOH$.

Under ordinary conditions slight ionization takes place with the formation of NH_4^+ and OH^- ions (see diagram 4.56). Because of this slight ionization, in which ammonia acts as a proton acceptor, ammonia is classified as a weak base.



4.56

4.57. Properties and Uses of Ammonia

a. Conduct ammonia gas through a glass tubing to the bottom of a tall cylinder filled with water. Point out the decrease in the size of the bubbles as they rise. Set up an ammonia fountain as shown in diagram 3.19, with phenolphthalein solution added to the water (see reference *4R-31*).

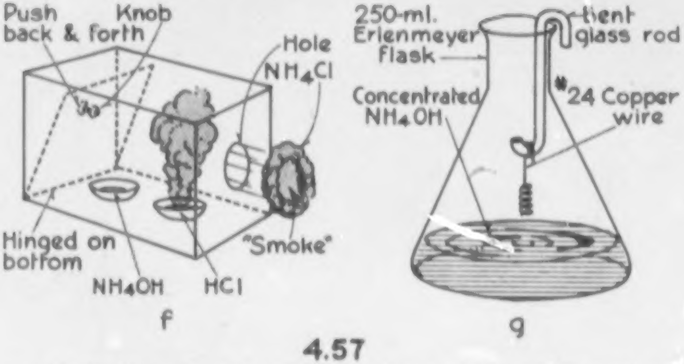
b. Ammonia diffuses rapidly due to its low molecular weight. Fill a large balloon with the gas. After rising initially, the balloon will sink due to diffusion through the rubber membrane.

c. Liquefy ammonia gas by running the gas into a thermos bottle filled with cracked dry ice in a hood. Pour the liquid ammonia into a small beaker and stand a small container of water in it; ice forms. Discuss the use of ammonia for refrigeration. *CAUTION: Do not form liquid ammonia by methods that involve pressure because of the danger of explosion.* See reference *4R-32.*

d. A major use of liquid (anhydrous) ammonia is direct application to farmland. The ammonia is needled into the soil from tanks. Set up two large flasks filled with ammonia gas. To one add a spoonful of good soil and shake. Compare the odor in the two flasks cautiously. Ammonia is readily absorbed into soils and other colloidal materials.

e. Discuss the "umbrella" vibration of the ammonia molecule with the aid of a molecular model. For the application of this vibration to highly accurate atomic clocks, see reference *4R-33.*

f. Prepare a smoke ring box as shown in the diagram 4.57*f*. Place evaporating dishes of ammonium hydroxide and hydrogen chloride inside the box. Allow a minute for the vapors to unite before operation. The smoke rings can be made to travel the length of the room. Discuss the formation of a characteristic "haze" on the outside of bottles in the chemistry laboratory.



4.57

g. CAUTION: Do not demonstrate the catalytic oxidation of ammonia with oxygen because, if it fails to operate at first, a dangerously explosive mixture accumulates. Instead, place about 30 ml. of concentrated ammonia in a 250-ml. Erlenmeyer flask. Take a 12-inch length of bare copper wire (*B* and *S* gauge *No. 24*) and wind a coil about ½ inch in diameter at one end. Attach the other end to a bent glass rod as in diagram 4.57g, so that the coil does not touch the liquid. Heat the coil of wire until red hot and quickly insert the oxidized copper into the flask. Due to the exothermic reaction between ammonia and oxygen being catalyzed on its surface, it will heat up, remain hot and sometimes melt. Bits of copper or copper oxide that fall into the liquid will react with the nitric acid to form Cu^{++} and with ammonia to form the blue complex ion $[Cu(NH_3)_4]^{++}$. Allow the reaction to continue for quite some time, then test the liquid for the nitrate ion. Discuss the use of liquid ammonia and "Lox" in rocket planes.

4.58. Test for the Ammonium Ion

a. To an unknown solid or solution add a concentrated sodium hydroxide solution and heat gently. Test the gas evolved with *moist* red litmus paper. If the litmus paper turns blue there is evidence that the unknown contained the ammonium ion. Ammonia gas is the only common gas which will react with moist litmus to produce a basic reaction. This is the basis of a famous quantitative test for nitrogen, the Kjeldahl method (see reference *4R-34*).

b. Add a few drops of ammonia water to a solution of copper sulfate. A white precipitate of copper hydroxide will form. Addition of more ammonia will cause the precipitate to redissolve, due to the formation of the intensely blue complex ion, $[Cu(NH_3)_4]^{++}$.

4.59. Production of Carbon

a. Show that many common substances are potential sources of carbon. Place table sugar (sucrose) in a dry 400-ml. beaker to a depth of one inch. Add about 200 ml. concentrated sulfuric acid. In about two minutes a ***steaming*** column of black porous carbon rises in the beaker. The delay is due to a slow buildup of heat as the acid extracts water (formed from—OH and—H groups on the sugar molecule) and combines with it. Damp sugar will react faster because water is available for the exothermic reaction with the acid. Concentrated solutions of sugar react with dangerous speed. Partly oxidized sugar molecules create the "burnt caramel" odor.

Submerge the carbon mass in a sink full of water to wash out the acid and rinse, break into pieces, rerinse and pass to the pupils for examination. When dry it can serve as "activated charcoal." Spent carbon can be reactivated by covering it with distilled water in a beaker and boiling completely dry.

b. Place a conical pile of magnesium turnings *(not powder)* 1 inch high and 3 inches in diameter on a piece of clean, dry asbestos. Ignite at the top with a bunsen burner. Poor circulation of air retards the combustion; blow *cautiously* at the pile to show this. From a tank or efficient generator play a stream of dry carbon dioxide on the pile through a piece of 6-mm. glass tubing. *CAUTION: The reaction accelerates.* When the reaction ceases, allow the mass to cool. Break open the pile to show that under the white oxide crust there is a considerable deposit of black carbon.

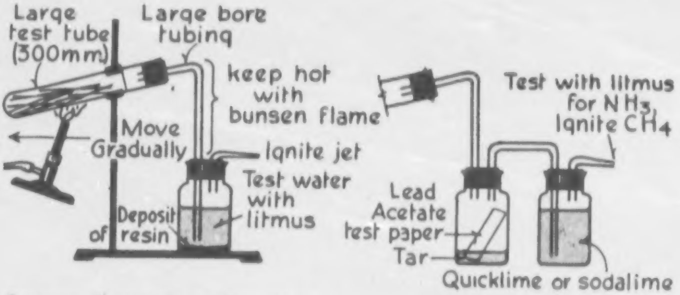
c. Adjust a bunsen burner to produce a sooty carbon flame and show that soot will collect on cool objects held in the flame. Show that it is easier to collect soot from a candle flame, and ask the pupils to explain why. The bunsen burner heats the object rapidly. Burning camphor, turpentine or naphthalene on a spoon will produce a very sooty flame.

Note: Some natural gas burners supplied when the community converted to a new gas supply may not produce a carbon flame unless masking tape is placed around the air inlet areas.

d. Perform destructive distillation of soft wood. Show that combustible gases, water soluble liquids, insoluble resins and nonvolatile carbon will form. See diagram **4.59*d*.**

e. For destructive distillation of coal see diagram 4.59*e*. A piece of moist lead acetate test paper stuck to the inside wall of the first bottle will detect H_2S. Perform the litmus test shortly after heating has begun, NH_3 and H_2S pass off quickly.

Note: Do not attempt this as a large-scale project. A considerable portion of the nitrogen in coal is liberated as the deadly gas, hydrogen cyanide.


Large test tube (300mm)
Large bore tubing
keep hot with bunsen flame
Move Gradually
Ignite jet
Test water with litmus
Deposit of resin
Test with litmus for NH3, Ignite CH4
Lead Acetate test paper
Tar
Quicklime or sodalime

SPLINTS, SHAVINGS OR SAWDUST

d

SOFT COAL

e

4.59

4.60. Properties of Carbon

a. Solubility. Show the insolubility of carbon by shaking lumps of charcoal in test tubes containing water, CCl_4, an acid and a base. Molten iron is, in a general sense, a solvent for carbon.

b. Adsorption. Fill a dry flask with ammonia and test with litmus. Add a spoonful of boneblack, stopper and shake flask for a few seconds. This mixture gives negative test with litmus. Mention its use as a deodorant in animal feeds. Review activity 3.55.

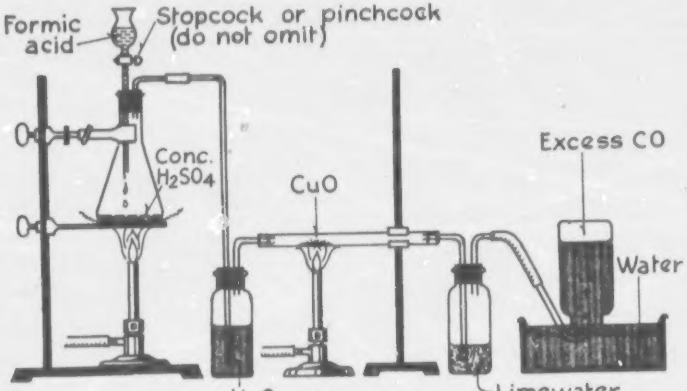
c. Reducing. Mix equal quantities of powdered charcoal and the "wire form" of cupric oxide in a pyrex test tube. With a one-hole stopper and delivery tube conduct the gas into a test tube containing limewater. Heat the solids strongly. The limewater turns milky. Have pupils write the equation. Remove the delivery tube from the limewater before heating is stopped. Pour the reaction mixture into a beaker of water and examine for the presence of copper.

Point out that, in the reduction of iron oxide and in some other reactions, the carbon is first converted to carbon monoxide which is the actual reducing agent.

4.61. Preparation of Carbon Monoxide

TEACHER DEMONSTRATION ONLY: Diagram 4.61 illustrates the preparation and the reducing ability of carbon monoxide. The equation for this reaction is:

$$H_2SO_4 + HCOOH \rightarrow CO + H_2SO_4 \cdot H_2O$$



4.61

The excess CO should be burned after removing the collecting bottle from the trough. *CAUTION: When taking the apparatus apart, burn the CO remaining in each section of the apparatus.*

Note: Sulfuric acid will also release carbon monoxide from oxalic acid and ferrocyanide salts.

4.62. Carbon Monoxide Poisoning

Pupils should receive practical information regarding the toxicity of carbon monoxide.

- Carbon monoxide is colorless, odorless gas. The odor of automobile exhaust fumes is due to some hydrocarbons that have been only partially oxidized.
- Automobile exhaust gases may contain 1 to 5 percent CO and this much is deadly. A concentration of one percent CO in air causes death in a few minutes, 1/10 of 1 percent causes death in an hour or so. Lawnmowers, outboard motors and gasoline generators present a hazard when operated indoors.
- The first symptom of CO poisoning is often a headache, due to a poor oxygen supply to the brain (anoxia); the second symptom is fainting. Chronic CO poisoning due to low levels of the gas is evidenced by minor headaches and lassitude.
- Carbon monoxide forms a compound with hemoglobin in a similar manner to oxygen:

$$\text{Hemoglobin} + O_2 \rightleftarrows \underset{\text{(red)}}{\text{oxyhemoglobin}}$$

$$\text{Hemoglobin} + CO \rightleftarrows \underset{\text{(brilliant red)}}{\text{carboxyhemoglobin}}$$

  The second reaction does not reverse readily, and the concentration of carboxyhemoglobin increases, tying up more and more hemoglobin. If a dose of CO is nonfatal, the body gradually restores the hemoglobin levels.
- The aerodynamic design of the rear end of automobiles and trucks may allow exhaust gases to enter the vehicle. The tailpipe should be directed into the air stream to avoid this. Driving an automobile with the trunk partly open can have the same effect.
- Incorrectly built or cracked chimneys have caused CO poisoning. Chimneys should rest on independent foundations to avoid damage as the building itself settles. In most localities it is against the law to use the chimney as any sort of support for the building.
- Carbon monoxide has the same density as nitrogen. It diffuses in air more rapidly than does carbon dioxide.

4.63. Preparations of Carbon Dioxide

a. Pupils should prepare this gas by the usual laboratory method of adding dilute hydrochloric acid to marble chips. The gas may be collected by displacement of water due to its low solubility at room temperature and pressure. Demonstrate the operation of a Kipp generator.

b. Dry ice is sometimes a convenient source of carbon dioxide. Dry ice may be available from warehouses and stores that specialize in frozen foods. A simple wooden box lined on all sides with an efficient insulator such as vermiculite will preserve dry ice for days. Do not make the lid tight because the gas should be allowed to escape. *CAUTION: Use tongs or gloves when handling it.*

Drop a piece of dry ice into a beaker of water containing brom thymol blue, or test the water with litmus paper.

c. Gently heat dry sodium bicarbonate in a test tube and conduct the gas through limewater. The testing of various carbonates and bicarbonates is an excellent pupil project. *Note:* Some carbonates do not decompose at temperatures available in the laboratory, especially if dry and pure.

d. An interesting pupil project is the determination of the CO_2 content of various baking powders. Weigh 3 gm. of each type of baking powder. Wrap each sample of powder in fine tissue paper and insert under separate cylinders of water inverted in a water trough containing a saturated solution of NaCl. Carbon dioxide is less soluble in salt water. The volume of the water displaced by the liberated CO_2 in each cylinder is a measure of the carbon dioxide producing ability of the baking powder tested.

4.64. Properties of Carbon Dioxide

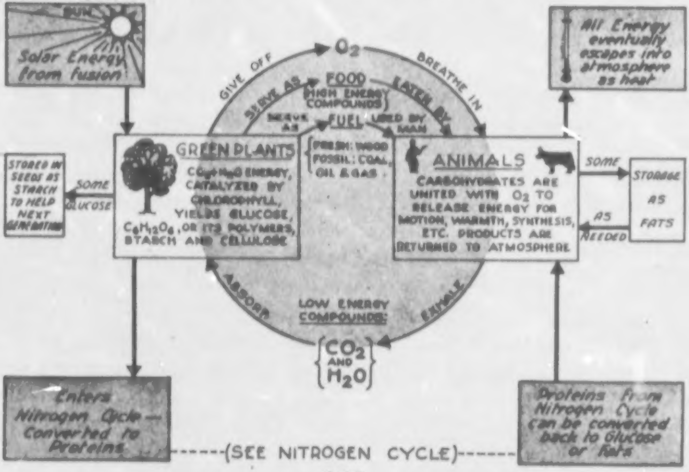
a. Set a burning candle about 4 inches high in a large beaker somewhat higher. Fill a similar large beaker from the CO_2 tank by upward displacement of air. Carry the "empty" beaker to the candle and pour it slowly down the inside of the beaker so that the candle burns until the CO_2 rises and "drowns" it.

b. Use the overhead projector to demonstrate the formation of calcium carbonate and calcium bicarbonate. Drop a piece of dry ice into a cylinder of limewater. A precipitate forms, then dissolves due to formation of soluble calcium bicarbonate. Other sources of CO_2 such as the bottled gas may be used.

4.65. Carbon Dioxide Cycle

The carbon dioxide cycle provides an opportunity to organize the relationships among many chemical reactions (see diagram 4.65).

THE CO_2-ENERGY CYCLE


SUN
Solar Energy from fusion
All Energy eventually escapes into atmosphere as heat
O_2
GIVE OFF
BREATHE IN
SERVE AS
FOOD (HIGH ENERGY COMPOUNDS)
EATEN BY
SERVE AS
FUEL
USED BY MAN
FRESH: WOOD
FOSSIL: COAL, OIL & GAS
STORED IN SEEDS AS STARCH TO HELP NEXT GENERATION
SOME GLUCOSE
GREEN PLANTS
CO_2+H_2O+ENERGY, CATALYZED BY CHLOROPHYLL, YIELDS GLUCOSE, $C_6H_{12}O_6$, OR ITS POLYMERS, STARCH AND CELLULOSE
ANIMALS
CARBOHYDRATES ARE UNITED WITH O_2 TO RELEASE ENERGY FOR MOTION, WARMTH, SYNTHESIS, ETC. PRODUCTS ARE RETURNED TO ATMOSPHERE
SOME
STORAGE AS FATS
AS NEEDED
ABSORB
EXHALE
LOW ENERGY COMPOUNDS:
CO_2 AND H_2O
Enters Nitrogen Cycle— Converted to Proteins
Proteins from Nitrogen Cycle can be converted back to Glucose or fats
-----(SEE NITROGEN CYCLE)------

4.65

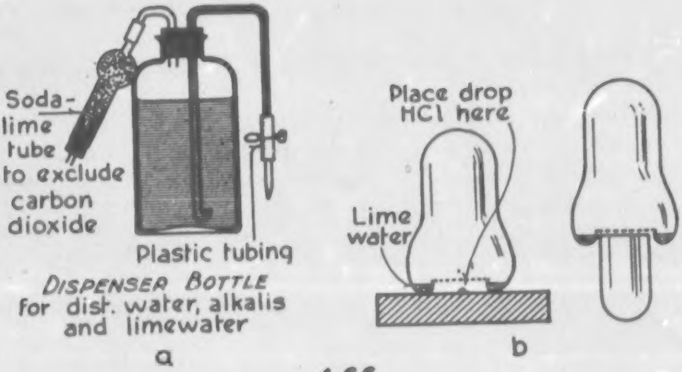
4.66. Carbonates and Bicarbonates

a. To test for the presence of the carbonate or bicarbonate ion, add a small amount of dilute hydrochloric acid to the compound to be tested. Pour or otherwise direct the gas into a test tube of *freshly* prepared limewater. Note the color change. Filtered limewater may be protected from atmospheric carbon dioxide as shown in diagram 4.66*a*.

b. For a convenient semimicro vessel that can be used to test minerals or placed over the mouth of a test tube to test solutions, see diagram 4.66*b*.

c. Prepare test tubes containing dilute solutions of Cu^{++}, Ni^{++}, Co^{++}, Sr^{++}, Ba^{++}, K^{+} and Na^{+}. Add a few drops of aqueous sodium carbonate solution to each. Insoluble carbonates form in five cases indicating that sodium and potassium carbonates are exceptional in their solubility. See the table of solubilities on page 336.

d. To illustrate the conversion of bicarbonates to carbonates prepare a dilute solution of $NaHCO_3$ and divide into two equal portions. To one portion add an equal volume of distilled water. Boil this solution until it has been reduced to the original volume. Carbon dioxide is escaping during the boiling process. Add dilute H_2SO_4 to both solutions; measure the amount of carbon dioxide evolved by collecting it over a saturated solution of NaCl. The unboiled portion contains twice as much gas. Explain by use of equations.


Soda-lime tube to exclude carbon dioxide
Plastic tubing
DISPENSER BOTTLE for dist. water, alkalis and limewater
a
Place drop HCl here
Lime water
b

4.66

4.67. Silicon

a. Preparation of Silicon. *TEACHER DEMONSTRATION ONLY:* A small sample of the free element may be prepared as follows. Mix thoroughly 1 gm. of magnesium powder with 2 gm. of the purest silica available in *dry* powdered form (powdered quartz is good). Place the mixture in a test tube small enough so that it is nearly filled, and tap gently on the table to consolidate the material. Hold the tube with tongs and heat the mixture near the top. As the reaction proceeds and the mixture glows, follow the glow with the flame to the bottom of the tube. When cool, transfer the product in small portions into 20 ml. of 1:1 hydrochloric acid. The acid will dissolve the magnesium oxide, and any magnesium silicide (Mg_2Si) that forms as a byproduct will decompose into a mixture of silicon hydrides. As bubbles of silicon hydrides emerge, a few harmless explosions occur as they ignite on contact with air:

$$SiH_4 + 2O_2 \rightarrow SiO_2 + 2H_2O$$

Heat the acid just to boiling and remove the beaker from the source of heat. When effervescence ceases, separate the fine crystals of silicon by filtration. Press the silicon powder between filter papers to dry it partially, and exhibit to the class. Save the material for use in activity 4.70.

b. Uses of Silicon and Its Compounds. Silicon makes up about 28 percent of the earth's crust and is the second most abundant element. Research in the chemistry of silicon is a frontier area. Modern technology has found some interesting uses for this abundant element and its compounds.

- Crystals of silicon are being used to make transistors and solar batteries.
- Vycor glassware (96 percent silica) can withstand extreme changes in temperature without breaking. This glassware is much cheaper than pure quartz glassware.
- Silicones, polymers in which the "backbone" is a chain of alternating silicon and oxygen atoms, are used to make silicone rubber, resins, oils and water repellants.

4.68. Silicic Acid Gels

Silicic acid gels are colloids which provide a medium in which reactions can occur.

a. **Preparing the Gel.** Dilute sodium silicate solution (water glass) to a specific gravity of 1.06, and dilute acetic acid to a concentration of 1 Normal (about 6 percent). See activity 3.29 for directions on making normal solutions. Mix the acid and water glass, and let the mixture set. Since the ratio of acid to water glass determines the setting time of the gel, the pupil should determine the ratio with which he can work most conveniently.

Compare the setting time of gels containing different amounts of acid. Vary the amount of acid by increasing the acid volume 1 ml. for each gel made. Decrease the amount of water glass by a corresponding amount so that the total volume of gel remains constant. Setting times vary from a few seconds to several hours. Graph the results. Note that a linear relationship is not involved.

b. **Making Gels by Using Other Acids.** Use equal volumes of different acids of the same normality to prepare the silicic acid gels. Compare the setting times of the gels.

c. **Lead Iodide Crystals.** In the acetic acid to be used to make the gel in activity 4.68*a*, dissolve enough solid lead acetate to give a concentration of about 1.5 gm. per ml. of gel. Pour the "water glass" *into* the lead acetate-acid mixture, stir, and pour the mixture into a tall glass cylinder. Let the gel set. Cover the gel to a depth of several centimeters with 2 normal potassium iodide solution (about 33 percent). Stopper the cylinder, and let it set for several days.

d. **Lead Tree.** Prepare the gel as in activity 4.68*c* above. Into the surface of the gel, place a small piece of zinc. Stopper the cylinder to prevent evaporation from the gel. A lead tree will be formed in a week or two.

e. **Rhythmic Precipitation.** Dissolve enough potassium dichromate in the acetic acid so there will be 1 gm. of the salt per 100 ml. of gel. Pour the acid *into* the water glass, stir, and let the gel set. Then cover the gel with 0.5 normal copper (II) sulfate to a depth of several centimeters. Stopper the container, and let it set for several days. A series of colored rings, Liesegang Rings, will be formed.

Vary the concentration of the chromate and copper sulfate. Study the differences in the bands and rate of formation.

Variations in banding experiments are reported in most colloidal chemistry texts and manuals.

4.69. Silicate Gardens

An interesting application of colloid chemistry can be demonstrated. In a 1,000-ml. beaker stir 100 ml. of a commercial "water glass" solution and 400 ml. of water. Add enough clean sand to form a thin layer covering the bottom. Drop in one crystal each of soluble salts of the following metals: Cu, Co, Pb, Fe, Ni, Mn and Ca. Within a few minutes a "chemist's garden" begins to grow, forming beautifully colored silicates. Let it stand quietly overnight. To preserve the garden, gently siphon off the silicate solution and replace with clear water.

All the above compounds hydrolyze in water. Copper sulfate hydrolyzes according to the following reaction:

$$CuSO_4 + 2H_2O \rightarrow Cu(OH)_2 + H_2SO_4$$

The sulfuric acid formed in this hydrolysis reacts with the sodium silicate (water glass) as follows:

$$H_2SO_4 + Na_2SiO_3 \rightarrow Na_2SO_4 + H_2SiO_3$$

The positively charged colloidal $Cu(OH)_2$ causes the negatively charged silicic acid to coagulate as a film of silicic acid gel. Some water from the "water glass" mixture seeps through the film of silicic acid gel and comes in contact with the copper sulfate, where hydrolysis is resumed again, and more copper hydroxide and sulfuric acid are formed. The products of hydrolysis, H_2SO_4 and $Cu(OH)_2$, then diffuse outwardly through the film of silicic acid gel and come in contact with the sodium silicate again to form more silicic acid gel. The process continues in this manner and thus gives rise to a phenomenon which appears similar to plant growth. The green color of the filament is due to cupric compounds which are formed during the process.

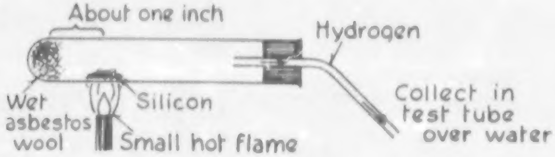
4.70. Reaction of Silicon with Steam

Place a plug of wet asbestos wool in the bottom of a large pyrex test tube. Carefully add a small quantity of the element silicon (from activity 4.67*a*) to the test tube while keeping the tube in an almost horizontal position. Set up the apparatus as shown in diagram 4.70. When heat is applied, the following reaction takes place:

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

A proper support must be provided for the test tube. Collect the gas produced in a test tube over water.

CAUTION: Remove end of delivery tube from water before removing source of heat. Test for hydrogen.

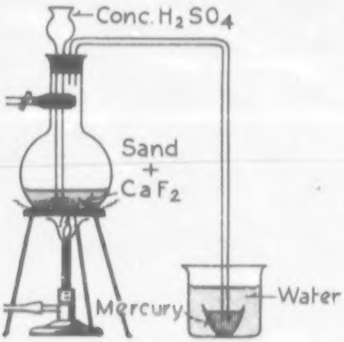

About one inch
Hydrogen
Wet asbestos wool
Silicon
Small hot flame
Collect in test tube over water

4.70

4.71. Action of Hydrofluoric Acid on Silicon Dioxide

TEACHER DEMONSTRATION ONLY: Place 4 gm. of calcium fluoride and a small amount of sand in a 500-ml. Florence flask. Use an old flask since hydrofluoric acid and hydrogen fluoride gas will attack glass. Arrange the apparatus as shown in diagram 4.71. *CAUTION: Use the hood. Great care must be taken during the demonstration and afterward, when cleaning the equipment, not to inhale hydrogen fluoride gas because it is very poisonous. Do not let the hydrofluoric acid come in contact with the skin since very serious and painful sores may result.*

Add sufficient concentrated H_2SO_4 (2 parts commercial acid to 1 part water) to seal off the bottom of the thistle tube. Heat gently if


Conc. H_2SO_4
Sand + CaF_2
Mercury
Water

4.71

the reaction doesn't proceed rapidly enough. The sand will gradually disappear due to the following reactions:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$$

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

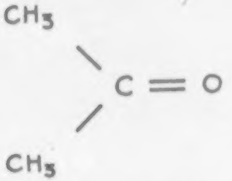
Note: At ordinary temperatures hydrogen fluoride gas may be composed of approximately equal amounts of H_2F_2 and H_6F_6 molecules. However, at higher temperatures the molecules of the gas have the formula HF.

The mercury trap is necessary to prevent water from entering the delivery tube and flask since SiF_4 is very soluble in water.

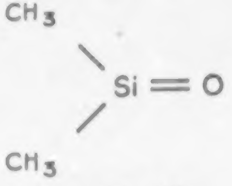
4.72. Silicones

In the decade following 1920 considerable progress was made in the preparation of large organic polymers by combining small molecules of carbon compounds into molecules having long chains. In the next decade, similar methods were applied in the preparation of large polymers from compounds of silicon. These polymers, known as "silicones" have many extraordinary properties.

The name "silicone" comes from a hypothetical analogy of its structure to that of a ketone such as acetone. Although a silicone does *not* have this simple a structure, this analogy is illustrated below:



ACETONE

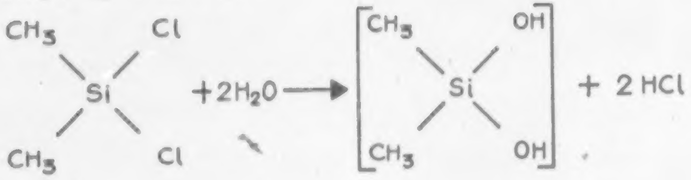


"SILICONE"

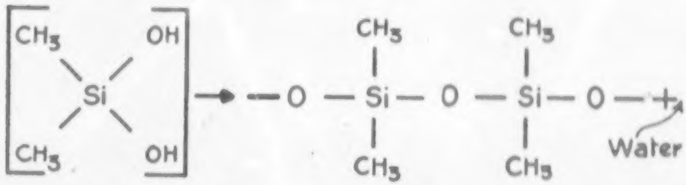
The following equations represent a simplified example of the preparation of a silicone when ether is used as a catalyst:

$$2CH_3Cl + SiCl_4 + 2Mg \rightarrow Si(CH_3)_2Cl_2 + 2MgCl_2$$

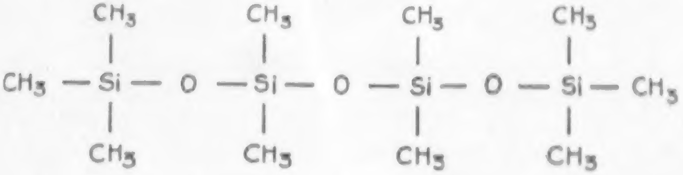
This unstable intermediate condenses intermolecularly to produce a repeating chain, as follows:



If several 'units' of the intermediary substance (dimethylsilanediol) react, the -O-Si-O- chain is increased thusly:



The structure of a typical silicone which may result is represented diagrammatically as:



$$\mathrm{CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3}$$

Many variations of the above reaction are used to regulate the length of chain, crosslinking of chains and nature of the organic groups attached along the chain. The number of possible types is unlimited. Continuing research in silicone chemistry represents a frontier in chemistry (see reference *4R-35)*.

Area 4 References

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NOTES

AREA 5

Ionization, Acids, Bases and Salts

5.01. Theory of Ionization

The topic of ionization may be introduced in a variety of ways, but one effective approach is from the standpoint of experimental evidences to support or at least suggest the need for a *theory of ionization.* Such experimental observations can be grouped to include a number of separate areas.

a. Electrical Evidence (Conductivity). Compounds whose water solutions conduct a current of electricity are called *electrolytes.* The passage of current is due to the presence of ions in the solution. In the case of an electrovalent compound, ions are already present in the substance and the placing of the substance in water merely provides an opportunity for the particles to dissociate and move about freely. Familiar salts such as sodium chloride, potassium nitrate and calcium chloride are examples of electrolytes that are electrovalent.

If the solute is a covalent compound, then the ions form as a result of the reaction between the solute and water as solution occurs. Hydrochloric acid, nitric acid and acetic acid are examples of covalent compounds which become electrolytes as a result of their molecules reacting with water. The extent to which such reaction occurs determines the conductivity of the electrolyte and the relative "strength" of the acid.

$$H_2O + HCl \rightleftarrows H_3O^+ + Cl^-$$

Equilibrium to the right (strong acid)

$$H_2O + HC_2H_3O_2 \rightleftarrows H_3O^+ + C_2H_3O_2^-$$

Equilibrium to the left (weak acid)

b. Abnormal Colligative Properties of Solutions. The unusual behavior of various solutions with respect to changes in such physical properties as boiling point, freezing point, vapor pressure and osmotic pressure is generally regarded as evidence in support for the theory of electrolytic dissociation. While Henry Cavendish was one of the first experimenters in this field, particularly in working with freezing point depressions, it remained for F. M. Raoult to note the pattern of behavior of various ionic substances whose solutions provided exception to the laws which predict change in colligative properties.

c. Rapid Reaction Rates. It is readily observable that reactions between electrolytes in solution occur virtually instantaneously.

Add 10 ml. of silver nitrate solution to 10 ml. of sodium chloride solution and observe how quickly a chemical change takes place.

There are many situations in which electrolytic substances will not react together at all when pure, but react immediately when placed in solution; baking powder is an example. Such reactions are in sharp contrast to reactions of solutions of nonelectrolytes which may take hours for substantial reaction to occur. Organic preparations, which for the most part involve nonionic substances, are characterized by such slow reactivity.

d. Properties Characteristic of Part of the Compound. Many ions manifest their presence in solution by certain characteristics which they impart to the solution. The color of the hydrated copper ion $Cu(H_2O)_4^{++}$, the sour taste of the hydronium ion (H_3O^+) and the slippery feel of the hydroxide ion (OH^-) are examples of such recognizable characteristics.

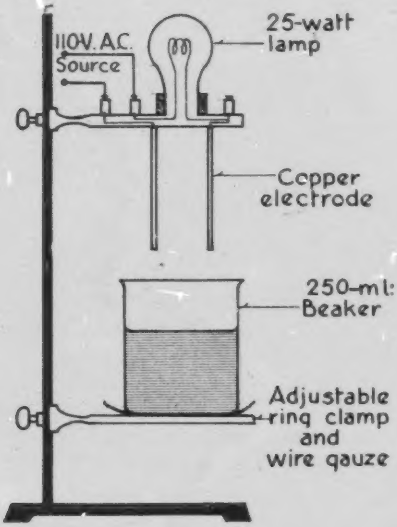
5.02. Conductivity of Solutions

The electrolytic property of solutions can be readily observed with a conductivity apparatus of either commercial or teacher-made origin.

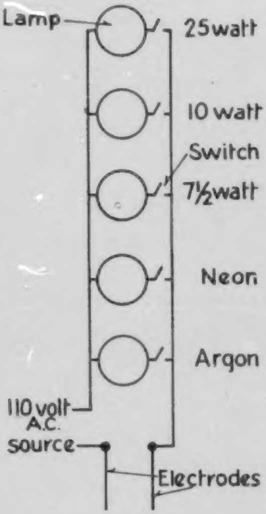
a. A simple and yet effective demonstration apparatus consists of a porcelain or plastic 120-volt lamp socket connected in series with copper wire electrodes (*B.S. gauge 16* or heavier is most satisfactory). If a variety of lamps is kept available for use in the apparatus, the observations can become more quantitative.

Diagram 5.02*a* shows the apparatus mounted on a ringstand and ready for demonstration use. If an adjustable support is used to hold the beaker containing the liquid to be tested, the depth of electrode immersion can be readily adjusted and controlled.

This type of apparatus can be used to test the conductivity of a great variety of substances. The use of a 25-watt lamp is recommended for most qualitative tests. Prepare solutions of various concentrations and similarly test. It is suggested that distilled water and 6M solutions of glycerol, ethanol, acetic acid, hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, potassium hydroxide and ammonium hydroxide be prepared and tested. Also test solutions of lower concentration, such as 0.1M, for solutions of acetic acid, hydrochloric acid, sodium hydroxide, ammonium hydroxide and sodium chloride. A great variety of substances and concentrations can be tested, but those indicated can give an adequate sampling for conclusions regarding types of compounds as well as concentrations and their effect on conductivity. If


110V. A.C.
Source
25-watt
lamp
Copper
electrode
250-ml.
Beaker
Adjustable
ring clamp
and
wire gauze

5.02a


Lamp
25watt
10 watt
Switch
7½watt
Neon
Argon
110 volt
A.C.
source
Electrodes

5.02b

the solutions are prepared in quantity, they can be bottled and stored for future use.

CAUTION: Because of the considerable shock hazard involved when operated from a 120-volt source, it is strongly recommended that the teacher demonstrate the various procedures involving the use of this apparatus. In the event a single pole switch is used, there is still the possibility of great shock hazard when the switch is in the off position. Teachers using the apparatus should disconnect the apparatus from the voltage source before touching the electrodes. The electrodes should be cleaned between each test by immersing them in a beaker of distilled water and wiping them dry with a clean paper towel.

b. A more sensitive apparatus which gives a higher degree of quantitative results may be permanently constructed. Prepare a bank of light sockets wired in parallel but with switches connected so that any one socket may be placed in or cut out of the circuit (see diagram 5.02*b*). Place in the sockets: an argon "glow" bulb, a neon "glow" bulb, a 7½-watt incandescent lamp, a 10-watt incandescent lamp and a 25-watt incandescent lamp. Place the apparatus in series with the electrodes in some manner such as shown in diagram 5.02*b*. The argon "glow" requires so little current that it will show the conductivity of glycerine, absolute ethanol, water and other very weak electrolytes, and will even discriminate between them by lighting to different degrees of intensity.

The neon "glow" requires more current, hence will identify somewhat stronger electrolytes.

The incandescent lamps can be used to differentiate the usual solutions and can be used in electrometric titrations. They will be extinguished one after another and then relight as the end point is reached and passed.

5.03. Effect of Solvent on Conductivity

a. Prepare a saturated solution of hydrogen chloride gas in toluene (or benzene) by mixing equal quantities (50 ml. of each) of concentrated hydrochloric acid and toluene in a separatory funnel. Shake the two liquids together thoroughly, allow them to separate and then obtain the desired hydrogen chloride-toluene solution. Using a 25-watt lamp, test the conductivity of this solution by placing it in a 250-ml. beaker and immersing the conductivity apparatus electrodes into the solution. Comparison of the result observed with that obtained using 0.1M hydrochloric acid solution indicates that not only the solute but also the solvent may be a factor in determining conductivity.

b. The dipole nature of water in contrast with most covalent organic solvents can be illustrated. Add 50 ml. of distilled water to the beaker containing the HCl-toluene solution. Stir, and again test for conductivity, making certain that the electrodes extend into the water layer.

5.04. Effect of Ion Removal on Conductivity

a. Place 50 ml. of 0.1N barium hydroxide solution in a 250-ml. beaker and arrange in position on the conductivity apparatus as described in activity 5.02*a*. While the current remains on, add slowly, and with constant stirring, 0.1N sulfuric acid solution. Add sulfuric acid until the lamp ceases to glow and note the appearance of the solution. The removal of ions by precipitation and water formation accounts for the observed result.

b. Place 50 ml. of 0.1N copper sulfate in a 250-ml. beaker and test this solution for conductivity. Slowly bubble hydrogen sulfide gas from an H_2S generator into the copper sulfate solution. Observe both the appearance of the solution and the behavior of the lamp. In this case while the reaction does remove cupric ions as insoluble cupric sulfide, the accompanying increase in hydronium ion concentration results in little or no change in the apparent conductivity of the solution.

5.05. Molten Salts as Conductors

a. *TEACHER DEMONSTRATION ONLY:* Half fill a *No. 0* porcelain crucible with potassium chlorate. Use the conductivity apparatus (see activity 5.02) to determine the conductivity of the solid salt. Place the crucible on the ringstand, supporting it with a triangle or ring of suitable size. *CAUTION: Be sure that chemicals of high purity and clean electrodes are used to avoid an explosion.* Carefully melt the potassium chlorate with a bunsen burner, and when it has melted immerse the electrodes of the conductivity apparatus into the molten salt. Evidence of dissociation is provided by the behavior of the fused salt as an electrolyte. Other salts, such as potassium nitrate and potassium thiocyanate, which also have relatively low melting points, can be used with equally good results.

b. An interesting demonstration can be performed using soft glass tubing of about 6-mm. diameter as the solid "salt." Place the electrodes of the conductivity apparatus about 1 cm. apart and use a 25-watt lamp. Place the soft glass tubing across the electrodes to show that the cold glass is a nonconductor. Heat a section of the tubing strongly in a bunsen flame until it becomes quite pliable. Quickly place the softened glass across the electrodes and observe the improved conductivity. Evidence of ionic movement in the "liquefied" glass is thus demonstrated. Best results will be obtained by arranging the apparatus so that the bunsen burner continues to heat the glass while it is in contact with the electrodes. The lamp will then burn continuously until the burner is removed.

5.06. Increase in Ion Concentration (Law of Mass Action)

Test the conductivity of solutions of 0.1N ammonium hydroxide and 0.1N acetic acid. These solutions will be found to be poor electrolytes because each has a relatively low degree of ionization.

After demonstrating the poor conductivity of separate solutions of ammonium hydroxide and acetic acid, place 50 ml. of each solution in a 250-ml. beaker, mix thoroughly and again test for conductivity. The higher concentration of ammonium and acetate ions as evidenced by the increased conductivity of the solution is an application of the Law of Mass Action. See also activity 9.08.

5.07. Colligative Evidence

a. Prepare solutions of cane sugar, table salt, calcium chloride and aluminum sulfate of approximately 0.5 molal concentrations. Appropriate quantities would be as follows:

17.1 gm. of sucrose per 100 gm. (or ml.) of water
5.5 gm. of calcium chloride (anhydrous) per 100 gm. (or ml.) of water
2.9 gm. of sodium chloride per 100 gm. (or ml.) of water

17.1 gm. of aluminum sulfate (anhydrous) per 100 gm. (or ml.) of water

Care must be taken if hydrated salts are used to give proper consideration to the change in calculated quantities required to produce solutions of 0.5 molal concentration. In the case of the aluminum sulfate, for example, if this is used as the typical crystal containing 18 water molecules for each aluminum sulfate "molecule," then a 0.5 molal solution would be obtained by dissolving 33.3 gm. of the hydrate in 83.8 gm. (or ml.) of water.

The freezing points of these solutions can be obtained with reasonable accuracy by placing 25 ml. of the solution in a test tube and cooling the mixture in a beaker of crushed ice mixed with rock salt. Stir the solution constantly and take thermometer readings in the solution until the solution is about half solidified. These solutions should differ sufficiently in freezing points so that the ordinary laboratory thermometer will readily detect significant differences. The difference between the sucrose and the aluminum sulfate is especially impressive, since the weights required to prepare 0.5 molal solutions are coincidentally identical.

b. A similar comparison can be made in the boiling points of the four solutions, although in this case the differences are significantly less because of the fact that the molal elevation of the boiling point of water is 0.52°C. whereas the molal depression of the freezing point is 1.86°C. When the procedure involving boiling point elevation is used, it is necessary first to determine the boiling point of pure water at the location involved. It is also desirable to prepare 1 molal solutions instead of the 0.5 molal solutions used for freezing point determination, since the more concentrated solutions will give a proportionally greater change in boiling point.

5.08. Characteristic Appearance of Ions

Early in the discussion on ionization, either coincidental with or subsequent to the comparison of atomic and ionic structure, it is well to demonstrate the difference in the appearances of masses of atoms and ions of the same species, and also the fact that certain ions can be readily identified by their characteristic appearance or behavior. Such a demonstration and explanation may help considerably in establishing the identity of ions as unique chemical units.

a. Display samples of sodium chloride, metallic sodium and chlorine gas. Discuss the considerable change in properties of both the sodium and chlorine when they unite and assume an ionic structure.

b. Show samples of anhydrous forms of cupric sulfate, cupric bromide and cupric chloride. Add water to a small quantity of each salt in separate large test tubes or beakers and observe the characteristic blue $Cu(H_2O)_4^{++}$ ion appearance from the salts which are quite dissimilar in appearance. Contrast the characteristic appearance of the cupric ion with the appearance of a sample of pure copper metal.

c. To any one of the solutions of Cu^{++} ions previously prepared, add sufficient ammonium hydroxide to obtain the copper-ammonia complex ion whose color is also characteristic of the specific ion species.

d. Other ions with characteristic colors can be demonstrated in solution. It is especially effective in preparing such solutions to start with anhydrous forms of the appropriate salts whenever possible. These could include such compounds as $CoCl_2$, Na_2CrO_4, $KMnO_4$, $FeCl_3$ and $Ni(NO_3)_2$. Pupils may be challenged to determine which portion of the compound is responsible for the color obtained. Observe various compounds in solutions to aid in drawing valid conclusions in this respect. For example, if the solution of sodium chromate is compared with solutions of sodium chloride and potassium chromate, the characteristic color of the chromate ion may be inferred.

5.09. Rapid Reactions Involving Ions

a. Observe the appearance of the dry salts of mercuric bromide and potassium iodide. Place approximately 1 gm. of each salt in a mortar and pestle and grind the mixture thoroughly. The orange color of mercuric iodide will form very slowly as a result of the metathesis reaction. If dilute solutions of the two salts are mixed in a large test tube or in a beaker, an instantaneous reaction occurs forming the HgI_2 as an orange precipitate. Some experimentation may be necessary in adjusting quantities and concentrations in this reaction, since it is possible to form a colorless and soluble complex ion.

b. Place small pieces of magnesium ribbon simultaneously into separate test tubes containing 1M hydrochloric acid and a HCl gas-toluene solution as prepared in activity 5.03. The rate at which hydrogen gas is evolved is suggestive of the presence of the ionic medium.

c. Compare also the rates of reaction of 1N hydrochloric acid and 1N acetic acid on pieces of magnesium, mossy zinc and calcium carbonate (marble chips). These observations should substantiate conclusions drawn from the conductivity experiments involving the same solutions.

d. Dissolve a few crystals of sodium chloride in a test tube half full of water. Add a drop of silver nitrate solution and note the time required for reaction. Add several additional drops of $AgNO_3$; note the speed of reaction. Contrast this rapidity of reaction with a typical organic reaction, such as the esterification of ethyl acetate from ethyl alcohol and acetic acid. *Note:* Time required for significant yield is 30 to 60 minutes.

5.10. Acids and Their General Properties

Acids are substances which supply the positive hydrogen ion (H^+). Since the hydrogen ion is a hydrogen atom nucleus and therefore simply a proton, acids may be defined as proton donors. This is the more general definition of an acid as proposed independently by the English chemist, T. M. Lowry, and the Danish chemist, J. N. Brönsted. According to this so-called proton theory not only molecules but also ionic particles may be regarded as acids. In water solutions the proton is attached to a water molecule forming the hydrated hydrogen ion (H_3O^+) called the hydronium ion.

a. Display samples of various acids such as sulfuric, hydrochloric, nitric, acetic, boric, oxalic, citric and tartaric acids.

b. React acid solutions of 6N concentration with metals such as magnesium, zinc and iron. Observe the distinction between strong and weak acids. Relate this to the degree of ionization.

c. Extremely dilute solutions (a few drops or crystals of acid in 20 to 30 ml. of water) can be prepared and safely tasted. The sensation of taste will be related to the degree of ionization, just as are other acidic properties. While some of the acids have already been tested as to electrical conductivity, this test can be repeated with a greater variety of acids to substantiate previous conclusions regarding acid "strength." In this connection it is of interest to note that a 0.0042N solution of hydrochloric acid would provide the same hydronium ion concentration as a 1N solution of acetic acid. These solutions are essentially identical in taste, conductivity and other acidic characteristics.

5.11. Bases and Their General Properties

While bases may be defined in terms of the hydroxyl ion in aqueous solution, the Brönsted-Lowry theory defines a base as a proton acceptor. According to this theory the OH^- ion is only one of many bases. The anions of all acids are classified as bases since they can react with the proton to form an acid molecule:

$$C_2H_3O_2^- + H^+ \rightarrow HC_2H_3O_2$$

The theory further states that, when water combines with the proton to form the hydronium ion, the water, in acting as a proton-acceptor, is a base.

a. Use extremely dilute solutions of such bases as sodium hydroxide, potassium hydroxide, calcium hydroxide and ammonium hydroxide to detect the characteristic bitter taste associated with bases. Concentrate the solutions only enough to obtain a perceptible taste sensation. *Note:* The difference between the sensations of sourness and bitterness cannot be readily described, and it is therefore desirable that pupils experience this distinction.

b. If the solutions of the various bases are of sufficient concentration to provide a taste sensation, then they should also be sufficiently concentrated to give the "slippery feel" which is associated with water solutions containing the OH^- ion.

5.12. Action of Acids and Bases with Indicators

Most acid-base indicators are weak organic acids and bases which undergo color changes when they are converted from their original essentially undissociated states to completely dissociated salts. The changes in color result from rearrangements in molecular structure which produce fundamental differences in electronic arrangement. Not only does each indicator have a typical color change, but such changes occur at certain definite ranges on the *pH* scale (see table below).

a. Place a few drops of each of the acidic and basic solutions in activities 5.10 and 5.11 on strips of both red and blue litmus. Ask pupils to describe results.

b. Show the effect of several of the acids and bases on other indicators such as methyl orange, phenolphthalein and congo red. This is especially effective as a demonstration. Add a few drops of the various indicators to these solutions of acids and bases arranged in a test tube rack.

c. Homemade indicators may be prepared from a variety of substances originating in nature. The effect of acidic and basic solutions on such substances as tea, red cabbage extract, grape juice and red radish extract can be readily tested. The latter can be obtained by boiling the skin of several red radishes in water, evaporating nearly to dryness and dissolving the residue, when cool, in a small volume of ethyl alcohol (95 percent). Pupils will find it interesting to test other plant extracts and flower pigments for possible use as indicators. They may be able to determine also the approximate *pH* scale region where color change occurs by comparison with other known indicators. The following table summarizes some common color changes.

INDICATOR	COLOR CHANGE	*pH* AT COLOR CHANGE
Methyl violet	green to violet	1.0
Methyl orange	red to yellow	3.1 — 4.4
Methyl red	red to yellow	4.0
Brom thymol blue	yellow to blue	6.0 — 7.6
Litmus	red to blue	5.0 — 8.0
Phenolphthalein	colorless to red	8.3 — 10.0
Thymolphthalein	colorless to blue	10.0
Alizarin yellow	yellow to violet	10 — 12

5.13. Hydrogen Ion Concentration (*pH*)

a. **Theory.** Although the concentration of acidic and basic solutions is readily expressed by molarity or normality, these methods are not especially convenient for very dilute solutions. Botanists and biologists, working with plant or animal fluids such as plant saps or blood, lymph and digestive juices, encounter very low alkaline or acid concentrations, which involve awkward decimals if expressed as normality or molarity. The *pH* system was devised for their needs but has been adopted also by chemists because of its usefulness.

The *pH* system is useful in describing the concentration of H^+ ions in solutions having a relatively small concentration of these ions. The term, *pH*, is defined as the logarithm of the reciprocal of the hydrogen ion concentration in a solution. For example, the H^+ concentration of pure water is 0.0000001M or 10^{-7}M. The reciprocal of 10^{-7} is 10^7 and its logarithm is 7. Therefore, the *pH* of pure water is 7.

The product of the concentration of H^+ ions and of the concentration of OH^- ions, $[H^+] \times [OH^-]$, is 10^{-14}. In the case of pure water the concentration of either the H^+ ion or the OH^- ion is 10^{-7}M, and the solution is neutral. If an acid is added to pure water, the H^+ concentration increases while the OH^- concentration must decrease. Conversely, if the OH^- concentration is increased by the addition of a base, the H^+ concentration must decrease since the product of the two concentrations is 10^{-14}.

To illustrate, a 0.1M solution of HCl is nearly completely ionized. It has an H^+ concentration of 10^{-1}M., or a *pH* of 1. Since $[H^+] \times [OH^-] = 10^{-14}$, the OH^- concentration is 10^{-13}M. This concentration may be expressed as a *pOH* of 13.

The following representation may assist pupils in understanding the mathematical relationship involved in *pH*.

pH		CONCENTRATION OF H^+ IN GRAMS PER LITER	EXPONENT
0	ACIDIC	1.	10^{0}
1		0.1	10^{-1}
2		0.01	10^{-2}
3		0.001	10^{-3}
4		0.0001	10^{-4}
5		0.00001	10^{-5}
6		0.000001	10^{-6}
7	NEUTRAL	0.0000001	10^{-7}
8	BASIC	0.00000001	10^{-8}
9		0.000000001	10^{-9}
10		0.0000000001	10^{-10}
11		0.00000000001	10^{-11}
12		0.000000000001	10^{-12}
13		0.0000000000001	10^{-13}
14		0.00000000000001	10^{-14}

The table indicates that, for any two solutions, the one having the lesser *pH* number has the higher concentration of H^+ ions. Differences between the *pH* of any two solutions by values of whole numbers such as 1, 2, 3, . . . represent differences in H^+ concentration by factors of 10, 100, 1,000, . . . Note that a solution of *pH* 6 contains 10^{-6} moles of H^+ ions per liter while a solution of *pH* 9 contains 10^{-9} moles of H^+ ions per liter. The solution of *pH* 6 contains 1,000 times as many H^+ ions per liter as a solution of *pH* 9. The numerical difference of *pH* is 3, which is the logarithm of 1,000.

Decimal differences in *pH* numbers represent differences in H^+ concentrations by factors which are not immediately obvious. The values must be obtained from tables of logarithms or antilogarithms. For example, a difference of 0.3 in *pH* numbers for two solutions indicates that the solution of lesser *pH* number has about twice the concentration of H^+ ions. Similarly, a difference of 0.6 in *pH* numbers indicates that the solution of lesser *pH* number has about four times the concentration of H^+ ions. See mathematical applications *3* and *4* below for explanations.

b. Mathematical Applications.

(1) *Determine the pH of a solution if the H^+ concentration is 0.00030M.*

$$pH = \log \frac{1}{.00030} = \log \frac{1}{3.0 \text{ x } 10^{-4}}$$

$$= \log \frac{10^4}{3.0} = \log 10^4 - \log 3.0$$

$$= 4.0 - 0.5 = 3.5$$

(2) *Determine the concentration of H^+ in a solution whose pH is 6.7.*

$$pH = \log \frac{1}{[H^+]}$$

$$6.7 = \log \frac{1}{[H^+]}$$

$$\log [H^+] = -6.7$$

$$= (-7 + 0.3)$$

$$[H^+] = 10^{0.3} \times 10^{-7}$$

See a table of logarithms for the number whose logarithm is 0.3. This is approximately 2.0, therefore, $[H^+] = 2.0 \times 10^{-7}$.

(3) *Compare the H^+ concentration of solution A (pH 6.7) with the H^+ concentration of solution B (pH 7.0).*

$$\frac{[H^+] \text{ for solution } A}{[H^+] \text{ for solution } B} = \frac{10^{-6.7}}{10^{-7}} = 10^{0.\text{[illegible]}} = 2$$

See a table of logarithms for the number whose logarithm is 0.3. This is approximately 2.

Therefore, solution *A* has two times the number of H^+ ions per liter as does solution *B*.

Note: This factor of 2 applies whenever the difference in any two *pH* numbers is 0.3.

(4) *Compare the H^+ concentration of solution A (pH 8.0) with the H^+ concentration of solution B (pH 8.6).*

$$\frac{[H^+] \text{ for solution } A}{[H^+] \text{ for solution } B} = \frac{10^{-8.0}}{10^{-8.6}} = 10^{0.6} = 4$$

See a table of logarithms for the number whose logarithm is 0.6. This is approximately 4.

Therefore, solution *A* has four times the number of H^+ ions per liter as does solution *B*.

Note: This factor of 4 applies whenever the difference in any two *pH* numbers is 0.6.

5.14. *pH* of Distilled Water

Test a sample of distilled water with a properly calibrated *pH* meter if such an instrument is available. If no *pH* meter is available determine the *pH* as accurately as possible with a *pH* paper, hydrion paper or universal indicator. Pupils are often surprised to find that the *pH* of distilled water usually tests substantially below *pH 7*, which they anticipate to be the result. Remove dissolved carbon dioxide from the distilled water by heating to boiling. The concentration should then be *pH 7*.

5.15. Preparation of Solutions of Known *pH*

Heat to boiling 500 ml. of distilled water in a clean flask. Cover the mouth of the flask with a small beaker and allow the water to cool. This boiled, distilled water can serve as a solution of *pH 7* and also for purposes of dilution. Prepare a 0.1M solution of HCl which can serve as a solution of *pH 1*. Dilute 5 ml. of this 0.1M solution with 45 ml. of the boiled distilled water giving a 0.01M solution which will be *pH 2*. Continue similar 1 to 9 dilutions producing solutions of *pH 3*, *pH 4*, *pH 5* and *pH 6*.

Starting with a 0.1M solution of sodium hydroxide, which has a *pH* of 13, prepare similar dilutions which would yield five additional solutions from *pH 12* to *pH 8*. Thus a complete range of approximate concentrations from *pH 1* to *pH 13* can be prepared for subsequent tests.

5.16. Color Change of Indicators

Place 5 ml. of each of the solutions prepared in activity 5.15 in a series of 13 clean test tubes. Add 2 drops of methyl orange indicator solution to each test tube, shake and observe the color change in each case. If the prepared solutions are of nearly correct concentration, the noticeable difference should be between solutions of *pH 3* and *pH 4*.

Test similar samples with other indicators, such as brom thymol blue, phenolphthalein and alizarin yellow. Again particular attention should be paid to the *pH* of the solutions at which the color change is noted.

It should now be possible to use these four indicators and approximate the *pH* of an "unknown" solution such as vinegar, lemonade or ammonium hydroxide solution (.05M). Pupils may find it interesting to prepare and check some of the solutions listed on the Reference Tables for Chemistry (see pages 333-336).

5.17. *pH* of Common Substances

Test various substances for hydrogen ion concentration. When soil samples are being tested, boil a little of the soil with distilled water in a beaker or large test tube and filter to obtain a clear liquid. Test this filtrate with universal indicator, hydrion or *pH* paper. Generally, the universal indicator gives the most satisfactory results. Other substances, such as toothpaste, soap, lemon juice and soft drinks, may be tested with the same indicators. The chart on page 205 will aid in identifying some of these substances.

A *pH* meter of one of the various types available is highly desirable for demonstration purposes. Such instruments, properly used, give results of much greater sensitivity and accuracy and can be utilized on many occasions in the chemistry laboratory.

5.18. Neutralization

The most important reaction of acids and bases, and one of the most important of all chemical reactions, is the neutralization reaction. This, by definition, is the combination of a hydronium ion and a hydroxyl ion:

$$\mathbf{H_3O^+ + OH^- \rightarrow 2H_2O}$$

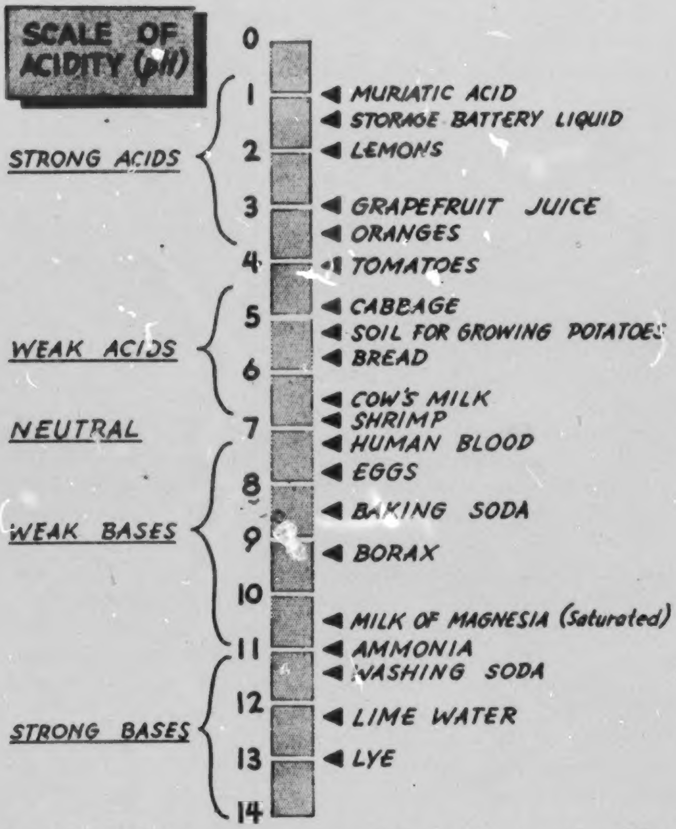
While this is the essential part of the reaction, there must be an additional product, since some anion must be associated with the hydronium ion as an acid and some cation with the hydroxyl ion as a base. The full neutralization reaction could then be represented as:

$$\mathbf{(H_3O^+ + A^-) + (B^+ + OH^-) \rightarrow 2H_2O + B^+ + A^-}$$

The byproduct of the reaction ($B^+ + A^-$) is called a salt. Salts are ionic substances which are typically strong electrolytes and exist in a great variety of cation-anion combinations.

This is the classical definition of acid-base reaction originated by Svante Arrhenius in 1887 which was broadened considerably by the Brönsted-Lowry Theory (1923). According to this theory, which defines an acid as a proton (H^+) donor and a base as a proton acceptor, many reactions can be included under the heading of neutralization which would not ordinarily be so classified, and media other than water may serve as solvents. Neutralization is thereby defined by the reactions

$$\mathbf{acid_1 + base_2 \rightarrow base_1 + acid_2}$$



in which case $acid_1$ and $base_1$ are called a conjugate acid and base pair and $base_2$ and $acid_2$ are likewise a conjugate pair. Typical reactions might appear as follows:

$$\begin{array}{ccccccc}
acid_1 & + & base_2 & & base_1 & + & acid_2 \\
H_3O^+ & + & OH^- & \rightarrow & H_2O & + & H_2O \\
H_2O & + & NH_3 & \rightarrow & OH^- & + & NH_4^+ \\
HCl & + & H_2O & \rightarrow & Cl^- & + & H_3O^+
\end{array}$$

As examples of neutralization reactions in nonaqueous media:

$$NH_4Cl + NaNH_2 \rightarrow 2NH_3 + NaCl$$

(in liquid ammonia)

$$HCl + CH_3COOK \rightarrow CH_3COOH + KCl$$

(in acetic acid)

The definition of acids and bases as stated by G. N. Lewis in 1923 (Lewis Theory) is even more general than the Brönsted-Lowry Theory. Whereas the latter theory limits the term acid to substances that possess hydrogen, the Lewis concept recognizes that other compounds may act similarly to acids when water is not present and should therefore be called acids. Lewis defines an acid as an ion or molecule that can accept electrons for covalent bond formation and a base as an ion or molecule that can donate a pair of electrons for covalent bond formation. Neutralization then becomes simply the formation of the coordinate covalent bond. The reaction

$$Ca(OH)_2 + H_2SO_4 \rightarrow 2H_2O + CaSO_4$$

would be classified as acid-base by all theories. The reaction between the anhydrides, however, would be neutralization only by the Lewis Theory.

$$CaO + SO_3 \rightarrow CaSO_4$$

Here the calcium oxide is the base because the oxide contributes the two electrons for covalent bonding. Sulfur trioxide is the acid, since it accepts the pair of electrons for sharing. Obviously a tremendous number of reactions fall into the acid-base classification if one accepts this theory.

a. Add a drop of phenolphthalein solution to about 10 ml. of water in a test tube, and then add a drop of dilute (1N) sodium hydroxide. Divide this solution between two test tubes and then add, dropwise, dilute (1N) hydrochloric acid to one test tube and dilute (1N) sulfuric acid to the other. This procedure may be repeated using various acids, bases and indicators to show a common pattern of results.

b. Place 10 ml. of 1N sodium hydroxide in an evaporating dish, add a drop of phenolphthalein, and then add 1N hydrochloric acid slowly and with stirring until the color just disappears. At this point the solution should be colorless, but one drop of base should turn it pink and one drop of acid should turn it colorless again.

Evaporate the colorless solution to dryness by placing the evaporating dish on a tripod or ringstand and heating carefully with a bunsen burner. When most of the water has been evaporated, the flame should be lowered. After the dry product has become cool, it can be safely tasted.

5.19. Nomenclature of Inorganic Compounds

The simplest compounds are the binary compounds, those consisting of two elements. In the case of the ionic compounds (salts) which are members of this group the *—ide* ending characterizes virtually all such compounds. If the metal which is involved in such combinations has a variable valence, the suffix *—ous* is used to denote the lower valence and the suffix *—ic* the higher valence.

Binary covalent compounds use the same *—ide* ending, but in the case of variable valence the prefixes indicating the number of atoms of the negative element are characteristically used. (Examples: sulfur dioxide, sulfur trioxide, carbon monoxide and carbon dioxide.)

Binary acids are characterized by the prefix *hydro-* and the suffix *—ic* as part of their acid names. The dependence of such compounds on the presence of water to display typical acid properties may be a helpful aid to remembering the nomenclature. However, it should be noted that the need for water for such assumption of acid properties is not unique among this group of compounds and is, in fact, generally characteristic of all acid compounds.

Many metals form compounds with hydrogen and oxygen which show basic properties and are classified as hydroxides. Both the naming and the formulas of such compounds follow simple principles of valence, which should offer no particular difficulty.

Most of the nonmetals and a few of the transition series metals form compounds with hydrogen and oxygen which are acidic. Among such compounds are carbonic, nitric, sulfuric and chromic acids (H_2CO_3, HNO_3, H_2SO_4 and H_2CrO_4). In a number of cases there is a series of acids which contains the same nonmetal with a variety of oxidation states. These compounds are distinguished from each other by the use of various prefixes and suffixes, including the following in the case of the nonmetal chlorine.

OXIDATION STATE OF CHLORINE	FORMULA OF ACID	NAME OF ACID	SODIUM SALT	NAME OF SALT
+1	$HClO$	Hypochlorous	$NaClO$	Sodium hypochlorite
+3	$HClO_2$	Chlorous	$NaClO_2$	Sodium chlorite
+5	$HClO_3$	Chloric	$NaClO_3$	Sodium chlorate
+7	$HClO_4$	Perchloric	$NaClO_4$	Sodium perchlorate

Probably the most important association for the beginning pupil in chemistry to make is the relationship between *—ous* acids and *—ite* salts and between *—ic* acids and *—ate* salts. Pupils who, for example, are familiar with the compound potassium chlorate should be able to name the acid $HClO_3$, even though this compound may be unfamiliar to them. The consistency in the names of the *hypo*— and *per*— acids and their corresponding salts may also be noted.

5.20. Preparing a Standard Acid

Stoichiometry. One of the most useful techniques of the analytical chemist is volumetric analysis in which the titration procedure is the fundamental operation. Since neither the equipment nor the mathematics which are involved in this procedure are at all complex, it is very appropriate that beginning chemistry pupils acquire an understanding of the principles involved.

Prepare a standard solution of oxalic acid by weighing as accurately as possible a sample of approximately 3.1 gm. of crystalline oxalic acid $(COOH)_2 \cdot 2H_2O$ (formula weight 126). If a 500-ml. volumetric flask is available, transfer the acid, without loss, to the flask and add sufficient distilled water to dissolve the oxalic acid. After the acid has dissolved, add sufficient distilled water to fill the flask to the calibration mark. The solution can then be transferred to a clean bottle or laboratory flask for storage. See activity 3.26. If no volumetric flask is available, satisfactory results can be obtained using an appropriate graduated cylinder for volume determination.

The normality of the acid solution can be calculated using the relationship:

$$\text{Normality of oxalic acid } (COOH)_2 \cdot 2H_2O = \frac{\text{Actual weight used (gm.)} \times 1{,}000 \text{ (ml).}}{63\text{(gm.)} \times \text{volume of solution(ml.)}}$$

Since 63 is the equivalent weight of the acid, a solution containing 63 grams per liter would be a 1N solution. If, for example, 3.1 gm. were contained in 500 ml., then by calculation

$$\text{N oxalic acid} = \frac{3.1 \text{ x } 1000}{63 \text{ x } 500} = 0.0098\text{N}$$

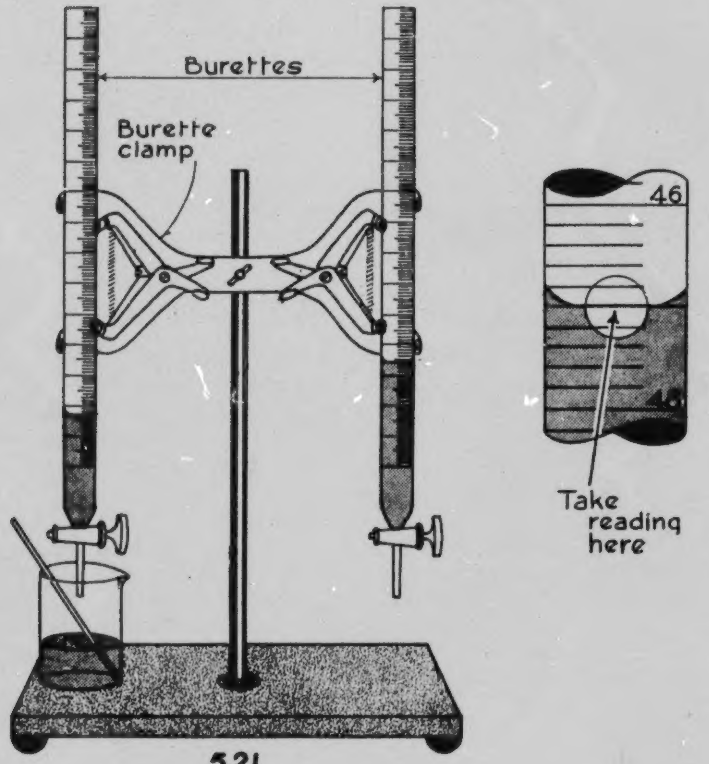
Since this standard solution was obtained by weight and volume measurement rather than by comparison with another solution, it may be termed a "primary standard."

5.21. Acid-Base Titration

A sodium hydroxide solution of approximate 0.1N concentration can be prepared by dissolving 2 gm. of NaOH in 500 ml. of distilled water. Sodium hydroxide is not appropriate for use in preparing a standard solution by weighing, since, being deliquescent, accurate weight determination is impossible. The prepared solution will be standardized by comparison with a standard acid solution.

A pair of burettes are necessary for this procedure, and these should be thoroughly cleansed and rinsed; first with distilled water and then with about 10 ml. of solution with which the burette is to be filled. Fill one burette with the standard acid and the other with the base to be standardized (see diagram 5.21). Fill the tip of each burette by opening the stopcock momentarily and letting a small amount of the solution flow through the tip into the beaker containing that solution. Add sufficient solution to the burette and adjust the liquid level so that the bottom of the meniscus is on the zero mark of the burette.

Remove about 15 ml. of base from the burette into a clean 150-ml. beaker. Add 2 drops of phenolphthalein and place the beaker under the acid burette. Add acid slowly and with constant stirring until the indicator color disappears. If too much acid is added, add more base,



5.21

drop by drop, until a faint color is restored. A white piece of paper under the beaker will make the color more perceptible. It should be possible to achieve the situation where 1 drop of acid will turn the solution colorless and a drop of base will produce a faint color. This is the end point of the titration.

Burette readings should then be taken and the normality of the base calculated from the relationship:

Normality of acid × Volume of Acid = Normality of Base × Volume of Base

or $N_A \text{ x } V_A = N_B \text{ x } V_B$. Inasmuch as the normality of the acid, the volume of the acid, and the volume of the base are known factors, it is possible to solve for the normality of the base. This solution may now be used in subsequent titrations where a standard base is required.

An example illustrating the use of typical data is shown below:

Volume of standard acid used in titration	24.3 ml.
Normality of standard acid	0.11 N
Volume of base used in titration	26.7 ml.
Normality of base determined by calculation	0.096 N

$$V_A \text{ x } N_A = V_B \text{ x } N_B$$

$$24.3 \text{ x } 0.11 = 26.7 \text{ x } N_B$$

$$0.10 = N_B$$

See reference *5R-1* for suggestions relating to the construction of titration graphs.

Reference *5R-2* contains a description of an investigation which provides for the study of some analytical procedures.

5.22. Importance of Proper Indicator in Titration

Dissolve 0.5 gm. of anhydrous sodium carbonate in 100 ml. of distilled water. Place 50 ml. of this solution into a 250-ml. beaker, add 2 drops of phenolphthalein, and titrate the solution with a standard solution of HCl of approximately 0.1N. Note the volume of the acid required to render the indicator colorless and calculate the normality of the Na_2CO_3 solution, based on this "end point." ($V_A \text{ x } N_A = V_B \text{ x } N_B$)

Now add 2 drops of methyl orange indicator to the unused 50 ml. of the Na_2CO_3 solution and titrate with the 0.1N HCl from the burette until an "end point" is reached, as is evidenced by the color change from yellow to red. Calculate the normality of the Na_2CO_3 solution based on the volume of acid used to achieve this end point. This makes an excellent problem demonstration, and at this point the pupils may be challenged to explain why the two different indicators give such dissimilar results, which are probably in an almost 2:1 ratio. *Note:* The more correct result may be inferred from the quantities used in preparing the original Na_2CO_3 solution.

The explanation, of course, lies in the fact that since the original Na_2CO_3 solution is approximately 0.1N, it has a *pH* of almost 12 and therefore turns phenolphthalein red. When enough acid has been added to change the original Na_2CO_3 to $NaHCO_3$, the *pH* will have become about 8.4, so a slight excess of HCl will cause the indicator to become colorless. In the case of the methyl orange indicator, however, the *pH* must be lowered to about 3.5 to obtain the color change. At this point the Na_2CO_3 will have completely reacted to yield NaCl, but twice the volume of acid will be required.

$$HCl + Na_2CO_3 \rightarrow NaHCO_3 + NaCl$$

$$2HCl + Na_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

Further discussion may establish the reason why phenolphthalein would be a satisfactory indicator when titrating a strong base with a weak acid, whereas methyl orange would be very unsatisfactory in this case. Similarly, methyl orange would be appropriate for use in a titration involving a strong acid and weak base and phenolphthalein would prove unsatisfactory. In a titration in which both the acid and base were strong, either indicator could be used. *Note:* Color change of phenolphthalein at *pH* 8.3 to 10; color change of methyl orange at *pH* 3.1 to 4.4.

5.23. Percent of Acetic Acid in Vinegar

A sample of vinegar (preferably white vinegar) can be titrated with the standard base by a procedure similar to that outlined in the preceding discussion and the normality of the solution of acetic acid determined. This normality can be converted into approximate percent concentration by determining the number of grams of acetic acid per 100 ml. of solution. This is a proportion wherein it is known that a 1N solution contains 60 gm. per liter (since 60 gm. is the equivalent weight of acetic acid). A 0.6N solution would, for example, contain 36 gm. per liter of solution or 3.6 gm. per 100 ml. Inasmuch as the density of vinegar is very nearly 1 gm./ml., this would represent an approximate 3.6 percent solution.

Similar procedures may be employed to prepare a standard HCl or H_2SO_4 solution, to determine the concentration of a sample of household ammonia or to determine the base strength of a solution of sodium carbonate.

5.24. Acid and Basic Anhydrides

a. The reactions of various nonmetallic oxides with water may be observed, but it will probably be necessary in each case first to prepare the oxide. In order to prepare some phosphorus pentoxide, place a piece of red phosphorus weighing about 0.5 gm. on an asbestos pad and ignite it with a bunsen burner flame or a piece of hot wire. Place a 250-ml. or larger beaker in an inverted position directly over the burning phosphorus. When the phosphorus has ceased burning, remove the beaker, place it right side up, and add 20 ml. of distilled water to it, swirling the water around the sides of the beaker in order to dissolve the phosphorus pentoxide which has collected thereon. Test the resulting solution with litmus in order to indicate the formation of phosphoric acid.

Prepare sulfur dioxide in a gas generator by the action of dilute sulfuric acid on sodium sulfite. Bubble the gas into distilled water for several minutes. Test the resulting solution for acidity.

Prepare carbonic acid either by using a gas generator containing limestone chips and dilute hydrochloric acid, or by merely bubbling exhaled air into distilled water for a few minutes.

In all the preparations described the distilled water used should first be tested to determine whether it is neutral or acidic. Quite frequently it is necessary to boil the distilled water just before using it in order to drive off the carbon dioxide which it has absorbed from the atmosphere.

b. The action of certain metallic oxides or peroxides may also be observed. Mix a small quantity (about 1 gm.) of calcium oxide with 50 ml. of distilled water in a 250-ml. beaker. *CAUTION: Be careful not to touch the calcium oxide with the fingers; it can produce a serious burn.* Test the resulting solution with litmus.

A similar result can be obtained by following the same procedure with magnesium oxide. If no magnesium oxide is available, it can be obtained by burning a 2-inch piece of magnesium ribbon and mixing the white oxide formed with a few ml. of distilled water in a test tube.

Mix a gram of sodium peroxide with 50 ml. of water in a beaker. In this case the evolution of oxygen gas will be noted as well as the formation of a basic solution as evidenced by the litmus test.

5.25. Hydrolysis

Hydrolysis may be broadly defined as the reaction of a substance with water. Many very important reactions of a hydrolytic nature occur, a large percentage of which require catalysis to produce a significant quantity of product. In the field of biological chemistry, for example, there are a great number of reactions of this nature.

The various reactions which occur when salts react with water provide additional application of ionic theory and fall within the definition of hydrolysis. Four cases may be distinguished, depending upon the electrolytic strength of the acid and base products: (1) Salt of a strong acid and a strong base (example is $NaCl$) forms a neutral solution with no hydrolysis; (2) salt of a weak acid and a strong base (example is $NaC_2H_3O_2$) forms a basic solution (*pH* above 7); (3) salt of a strong acid and a weak base (example is NH_4Cl) forms an acid solution (*pH* below 7); and (4) salt of a weak acid and a weak base (example is $NH_4C_2H_3O_2$) forms a solution which may be either acidic, basic or neutral, depending upon the ionization constants of the products.

a. Dissolve a few crystals of each of the following salts in distilled water in separate clean test tubes: cupric sulfate, potassium carbonate, ammonium chloride, sodium nitrate, sodium acetate, aluminum sulfate, barium nitrate, ammonium phosphate, potassium sulfate and calcium acetate. Test each of these solutions with red and blue litmus paper. *Note:* While litmus is a reasonably satisfactory indicator for this purpose, brom thymol blue solution, if available, is substantially more sensitive to solutions which are either weakly acidic or basic.

b. Prepare 0.1N solutions of aluminum sulfate, sodium bicarbonate, sodium carbonate and potassium chloride. If a *pH* meter is available, use this instrument to determine the *pH* of each of the prepared solutions. If no *pH* meter is available, test the solutions with universal indicator or hydrion paper.

Prepare an aqueous soap solution by dissolving approximately 2 gm. of toilet soap in 100 ml. of distilled water. Place 50 ml. of the soap solution in a 250-ml. beaker and add a drop or two of phenolphthalein. Add 50 ml. of 95 percent ethyl alcohol to this colored solution and stir. It becomes apparent that alcohol represses the hydrolysis of the soap solution. In order to show that the alcohol has not rendered the indicator inactive, add a few drops of 6N sodium hydroxide.

5.26. Buffer Action

There are many situations both in laboratory procedures and in the vital processes of living organisms where it is highly desirable for a solution to be able to resist changes in its *pH* value in spite of the addition of substances which may supply either hydrogen or hydroxyl ions. Solutions which are able to maintain a fairly constant *pH* under the conditions mentioned are called buffered solutions. Their ability to achieve such stability is, of course, related to their chemical composition.

The blood is an excellent example of a buffered solution. It retains a *pH* slightly above 7 in spite of the wide variety of foods which might be expected to change this slight alkalinity. In the case of the blood the buffering is accomplished mainly by carbonates, phosphates and proteins. In most cases a buffered solution consists of a weak acid or a weak base plus a salt of that weak acid or base.

An example may provide explanation of the mechanism of buffer action. The ionization of acetic acid can be stated as

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

which indicates that the equilibrium is strongly to the left, maintaining a high concentration of undissociated molecules. If sodium acetate is added to such a solution, the high degree of ionization of the salt would provide a much higher concentration of $C_2H_3O_2^-$ ions and a consequent reduction in the concentration of H^+ ions, forming more molecular acetic acid. This solution would now have a *pH* which would resist change. If, for example, a source of hydrogen ions were added to the solution, the acetate ions would combine with the hydrogen ions, keeping the hydrogen ion concentration very nearly the same.

$$H^+ + C_2H_3O_2^- \rightarrow HC_2H_3O_2$$

If, on the other hand, a base were added, the hydroxyl ions of the base would combine with some of the hydrogen ions to form water. This would make it possible for the equilibrium of acetic acid ionization to procede to the right, thus reestablishing the concentration of H^+ ions.

$$H^+ + OH^- \rightarrow H_2O \quad \text{(addition of base)}$$
$$HC_2H_3O_2 \rightarrow H^+ + C_2H_3O_2^- \quad \text{(results in dissociation)}$$

a. A buffer solution whose *pH* is approximately 7 can be prepared by dissolving 6.8 gm. of KH_2PO_4 in distilled water and adding 296 ml. of 0.1N NaOH. The resulting solution should be diluted to a volume of one liter.

To observe the buffer effect place 50 ml. of freshly boiled distilled water in one beaker and 50 ml. of the prepared buffer in another. Add 2 drops of phenolphthalein to each beaker and titrate each with 0.1N NaOH. A comparison of the quantities required to produce a similar coloration in each beaker, which represents a change in *pH* from 7 to about 9, illustrates the difference in stability of unbuffered water as contrasted with the buffered solution.

The titration procedure should be repeated, using methyl orange indicator in 50 ml. samples of freshly boiled distilled water and the buffer solution, this time titrating with 0.1N HCl (or other acid of similar concentration). This time a change in *pH* from 7 to approximately 3.5 is accomplished by a greater quantity of acid in the buffered solution than in the unbuffered water.

b. Prepare a buffer solution which consists of equal volumes of 1M sodium acetate and 1M acetic acid. Determine the *pH* of this solution using either a *pH* meter or an indicator method (hydrion paper or universal indicator).

Dilute a solution of hydrochloric acid sufficiently to produce a solution whose *pH* is as nearly the same as the buffer solution as possible. This will probably be approximately a 10^{-5} M solution of HCl.

Place 100 ml. of the buffer solution in one 250-ml. beaker and 100 ml. of the diluted HCl solution in a second beaker. Add 10 ml. of 1M sodium hydroxide solution to each beaker, stir thoroughly, and determine the *pH* of each solution by the same method used previously. While a lesser amount of sodium hydroxide solution could be used it should be possible to use this quantity without substantially affecting the *pH* of the buffer solution.

5.27. Common Ion Effect

The ionization of a weak electrolyte tends to decrease when an ionic compound containing one of the ions of the weak electrolyte is added to the solution. This phenomenon is called the "common ion effect."

If a salt of a weak base, such as ammonium chloride, is added to a solution of the weak base, ammonium hydroxide the increase in the concentration of NH_4^+ ions will cause a corresponding decrease in the OH^- ions, thus making the weak base even weaker. Similarly, if sodium acetate, which is the salt of a weak acid, is added to a solution of the weak acid, namely acetic acid, a decrease in the hydrogen ion concentration will be noted.

In a somewhat similar fashion the addition of a common ion affects the equilibrium of solutions of slightly soluble salts and reduces the solubility of such salts. This behavior is also referred to as the common ion effect and may find practical application in chemical analysis and separation.

a. Place about 200 ml. of distilled water in a 250-ml. beaker; add 2 drops of phenolphthalein solution and 25 ml. of concentrated ammonium hydroxide This solution contains sufficient OH^- ions to produce a fairly intense red color. Now stir into the solution some solid ammonium chloride, adding only a few crystals at a time and noting the change in color from red to pink which indicates the decrease in OH^- ion concentration.

b. Prepare 30 ml. of saturated silver acetate solution and divide the solution equally among three test tubes. To one test tube add a few crystals of silver nitrate, to the second a similar quantity of sodium acetate and to the third a like quantity of ammonium nitrate. In the first two instances the addition of a common ion disturbs the equilibrium of the system and causes precipitation, while in the third case no such precipitation occurs since no common ion has been introduced.

c. Prepare sufficient saturated solution of sodium chloride to nearly fill a 100-ml. graduate. If 45 gm. of sodium chloride are added to 100 ml. of distilled water, the mixture stirred thoroughly and the excess salt allowed to settle out, the clear liquid can then be decanted into the graduated cylinder.

Bubble hydrogen chloride gas into the saturated sodium chloride solution, using either a cylinder of HCl gas or an HCl generator. If the gas is prepared in a generator it is desirable that the gas be as dry as possible. The addition of concentrated hydrochloric acid to concentrated sulfuric acid in a generating flask will produce a satisfactory gas. Bubble the HCl gas into the solution until a noticeable quantity of salt has crystallized from the solution.

This effect is especially impressive, since no solid material is added nor is a reaction required in the solution to produce precipitation.

5.28. Migration of Ions (Electrolytic Diffusion)

TEACHER DEMONSTRATION ONLY: Nearly fill a battery jar or 1,000-ml. beaker with water and drop in a large crystal of copper sulfate. Observation over an extended period of time will indicate that the blue color of the $[Cu(H_2O)_4]^{++}$ ion diffuses very slowly throughout the solution.

To a second container of similar capacity add water and a large crystal of $CuSO_4$ as before. In this case introduce electrodes such as carbon rods into the solution, connecting the electrodes to a 6-volt battery or other source of direct current. Place the positive electrode near the $CuSO_4$ crystal and the negative electrode at some distance from the crystal. Some experimentation may be necessary to determine the most effective distance. A much more rapid diffusion of color occurs, due to the forces now acting on the $[Cu(H_2O)_4]^{++}$ ions.

5.29. Electrolysis

The passage of an electric current through certain molten compounds and electrolytic solutions is due to the presence of ions in such liquids. That these ions play an active part in such conductivity is a fundamental concept in the theory of ionization and distinguishes such conductivity from the conductivity of metals. With the latter it is assumed that the conductivity is related to the freedom of movement of some of the electrons in the structure of atoms, and the electric current is simply the movement of electrons from one atom to another.

Since ions are involved in the conduction of electricity through molten salts and electrolytic solutions, changes in the ions themselves must always accompany such conduction. The reduction reactions which occur at the cathode are an integral part of the conductivity process. The study of such electrolysis reactions offers opportunity either to introduce or find application for the concept of oxidation-reduction. It was Michael Faraday, one of the first to study electrolysis reactions, who introduced such terms as ion, anode, cathode, anion and cation.

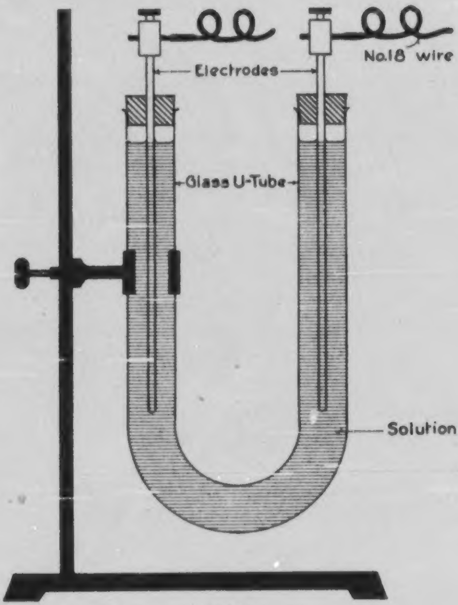
a. TEACHER DEMONSTRATION ONLY: The electrolysis of water is most effectively demonstrated with the Hoffman-type apparatus which is available in most laboratories. Since such an apparatus is usually equipped with platinum electrodes, it can be used effectively with a variety of solutions, including dilute sulfuric acid.

In order to demonstrate the electrolysis of water prepare a dilute solution of sulfuric acid which is approximately 1-molar. Such a solution is of sufficient concentration to cause the evolution of the gases at a fairly rapid rate if a direct current supply of 6 to 12 volts is used. In a quantitative observation of gas volumes, the volume of oxygen is less than half that of the hydrogen because of the greater solubility of oxygen in water. This difference can be minimized by allowing the initial samples of gases to escape and then collecting samples after the solution has become saturated with the gaseous products.

The hydrogen can be readily identified by allowing a few milliliters to escape into an inverted test tube and bringing the mouth of the test tube to a small flame. *CAUTION: Care should be taken not to place the splint near the hydrogen outlet.* A glowing splint, held above the opening of the stopcock on the side where the oxygen has collected, can be reignited several times by releasing small quantities of oxygen gas.

b. TEACHER DEMONSTRATION ONLY: The result of electrolyzing water with alternating current is of interest, especially if pupils are first asked to predict the result of such a reaction. The explanation of the result on the basis of ionic theory offers further evidence for the validity of the theory. The same equipment and solution may be used as in the preceding demonstration, substituting a low-voltage alternating current of 6 to 12 volts for the direct current previously used. Low-voltage substations or transformers may be used for this purpose. Since the mixture of gases produced on each side of the apparatus is highly explosive, it should be tested only after it has been removed into an inverted test tube. *CAUTION: Do not attempt to ignite the gas at either stopcock.* Pupils should be able to explain why such a mixture results and also why identical volumes of gases collect in both tubes.

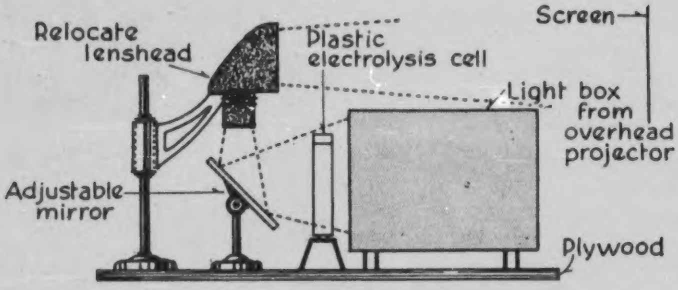
c. TEACHER DEMONSTRATION ONLY: A U-tube makes a suitable container for various electrolytic reactions and can be used for demonstration purposes if it is of adequate size (see diagram 5.29*c*). Prepare a saturated solution of NaCl and fill the U-tube with this solution, adding a few drops of phenolphthalein indicator solution. Use a 6- to 12-volt direct current supply, such as a storage battery, and electrolyze the solution for several minutes. This can be used as a "problem" demonstration, with pupils providing explanation for their observations. It will probably be necessary to continue the reaction for quite some time in order to collect a detectable sample of chlorine gas, due to its solubility in water.



5.29c

d. TEACHER DEMONSTRATION ONLY: Fill the U-tube with a concentrated solution of sodium sulfate, add a few drops of litmus solution, and electrolyze the solution with 6 to 12 volts d.c. After noticeable color change has occurred, reverse the terminals and note the gradual reversal of color. (The Hoffman apparatus can be used for this demonstration if more convenient, and only enough solution to completely submerge the electrodes need be added.)

e. The overhead projector may be modified slightly to produce an effective demonstration using a plastic electrolysis cell (see diagram 5.29*e*).



5.29e

5.30. Preparation of Iodine by Electrolysis

TEACHER DEMONSTRATION ONLY: Place a solution of potassium iodide in the U-tube apparatus and connect the electrodes to the 6- to 12-volt d.c. supply. In this case the action at the anode is clearly visible as "free" iodine is formed. The formation of potassium hydroxide at the vicinity of the cathode can be demonstrated by adding a few drops of phenolphthalein solution to the original solution to be electrolyzed. (The Hoffman apparatus may be used, if available.)

5.31. Oxidation-Reduction Reactions Involving Iron Compounds

a. An interesting yet simple demonstration to illustrate an oxidation-reduction reaction without oxygen is the change to iron (III) in the presence of potassium thiocyanate (KCNS). Add 1 ml. of KCNS solution to 25 ml. of iron (II) chloride solution. Next add 5 ml. of chlorine water. A deep red color indicates the presence of the iron (III) ions. *Note:* The iron (II) solution must be prepared fresh and protected from oxidation by atmospheric oxygen. Adding a few clean nails to the bottle containing $FeCl_2$ solution will help to keep the iron ions in the iron (II) state.

The iron has been oxidized (lost electrons) and the chlorine has been reduced (gained electrons) as indicated in the following equations:

$$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$$
$$2Fe^{++} - 2e \rightarrow 2Fe^{+++}$$
$$2Cl^{\circ} + 2e \rightarrow 2Cl^{-}$$

b. TEACHER DEMONSTRATION ONLY: Fill the U-tube electrolysis apparatus (or the Hoffman apparatus) with a saturated solution of ferric chloride which contains a few drops of potassium ferricyanide solution. If these solutions are freshly prepared, no color-change reaction should occur. Electrolyze the solution and note the reaction of the cathode which produces the precipitate $KFeFe(CN)_6 \cdot H_2O$ with its characteristic blue color. The color is produced as a result of Fe^{+++} ions being reduced to Fe^{++} ions at the cathode and reacting with the $K_3Fe(CN)_6$ as indicated in the following equations:

$$Fe^{++} + 2Cl^- + 3K^+ + Fe(CN)_6^{---} + H_2O \rightarrow$$
$$KFeFe(CN)_6 \cdot H_2O \downarrow + 2K^+ + 2Cl^-$$

By disregarding the ions which are not essential to the reaction, the equation becomes

$$Fe^{++} + K^+ + Fe(CN)_6^{---} + H_2O \rightarrow KFeFe(CN)_6 \cdot H_2O \downarrow$$

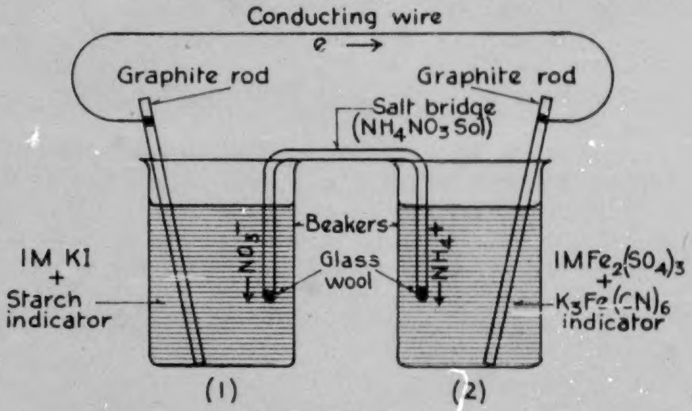
c. TEACHER DEMONSTRATION ONLY: A solution of ferrous ammonium sulfate which contains a small quantity of potassium thiocyanate solution can be electrolyzed in a U-tube to demonstrate the oxidation reaction at the anode. First demonstrate the value of KCNS solution as an analytical reagent to distinguish Fe^{++} from Fe^{+++} ions. Add a few drops of KCNS solution to solutions of ferric chloride and ferrous ammonium sulfate in separate test tubes. The deep red coloration, due to the formation of the ferric-thiocyanate complex-ion, is a positive identification for the presence of Fe^{+++} ions.

$$6\ CNS^- + Fe^{+++} \rightarrow Fe(CNS)_6^{---}\ \text{(red color)}$$

Note: When the solution containing both ferrous ammonium sulfate and potassium thiocyanate is electrolyzed, the deep red color appears at the anode, thus indicating the oxidation of ferrous ions to ferric ions.

d. Demonstrate an oxidation-reduction (*redox*) reaction in terms of an electron transfer by means of a half-cell reaction with indicators which produce a color change. Use this as a generalization to show that an *oxidizing agent* is a substance capable of accepting electrons. When it has acquired a prescribed number of electrons it is reduced. Likewise, generalize that a *reducing agent* is a substance capable of losing electrons. When it has lost a prescribed number of electrons it is oxidized.

Set up the apparatus as shown in diagram 5.31*d* and allow the short-circuited system to stand for a short time. A deep blue color in beaker *1* will indicate the presence of free iodine, and a blue color (Turnbull's blue) in beaker *2* will indicate the presence of iron (II). Since no oxidant was present in the beaker containing the potassium iodide solution and no reductant was present in the beaker containing iron (III) sulfate, a flow of electrons from one electrode to the other through the conducting is assumed. *Note:* A salt bridge may be prepared by


Conducting wire
e →
Graphite rod
Graphite rod
Salt bridge
(NH4NO3 Sol)
Beakers
Glass wool
NO3−
NH4+
IM KI + Starch indicator
IMFe2(SO4)3 + K3Fe(CN)6 indicator
(1)
(2)

5.31d

filling a U-tube with a strong salt, NH_4NO_3 (5 gm. in 20 ml. of H_2O). Place glass wool plugs in the ends of the U-tube, and quickly invert the ends of the tube into the beakers of solution.

Beaker *1* : $2I^- - 2e \rightarrow I_2$ (oxidation)

Beaker *2* : $2Fe^{+++} + 2e \rightarrow 2Fe^{++}$ (reduction)

5.32. Reduction of Stannous Chloride

TEACHER DEMONSTRATION ONLY: Prepare a solution of stannous chloride by dissolving 10 gm. of the compound in 100 ml. of water, and adding sufficient hydrochloric acid to produce a clear solution. Fill the U-tube with this solution and electrolyze it, using a carbon rod anode and a bare copper wire as the cathode. A 6-volt d.c. source should be adequate to produce a deposition of tin on the cathode within a reasonably short time.

5.33. Ionic Equations

On occasion the reaction between solutions of salts, such as sodium chloride and silver nitrate, are represented as:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$$

This equation does not accurately represent the true situation since it implies that the dry salts react. For Regents examination purposes ionic equations should indicate the nature of the ions, the charge on the ions, the reactions possible and whether the reaction is reversible. Any obvious method indicating these factors is acceptable, including the following:

(1) $Na^+ + Cl^- + Ag^+ + NO_3^- \rightarrow Na^+ + NO_3^- + AgCl\downarrow$

The AgCl is shown as un-ionized and as a precipitate which is essentially correct. Most of the Ag^+ and Cl^- ions leave the solution.

(2) $2Na^+ + CO_3^{--} + 2H^+ + SO_4^{--} \rightarrow H_2O + CO_2\uparrow + 2Na^+ + SO_4^{--}$

The moderately soluble carbon dioxide is shown as leaving the solution, and the reaction proceeds toward an end.

(3) $K^+ + OH^- + H^+ + Cl^- \rightarrow K^+ + OH^- + H_2O$

The relatively un-ionized water is here shown as un-ionized. If the slight ionization of water is to be represented a thinner (or shorter or dashed) arrow to the left should also be drawn.

(4) $2Na^+ + 2Cl^- + Ba^{++} + 2NO_3^- \rightleftarrows 2Na^+ + 2NO_3^- + Ba^{++} + 2Cl^-$

The double arrow indicates that the reaction is reversible.

5.34. Electronic Equations

The electrolysis of fused sodium chloride is often represented by the equation

$$2NaCl \xrightarrow{\text{elect.}} 2Na + Cl_2$$

The reactions involved are more clearly understood when they are expressed as *electronic equations*. One method of writing such equations is:

Reaction at the Cathode: $2Na^+ + 2e \rightarrow 2Na^\circ$

Reaction at the Anode: $2Cl^- - 2e \rightarrow 2Cl^\circ \rightarrow Cl_2$

It is immediately obvious that, at the cathode, the sodium ion gains an electron and is reduced. Similarly, at the anode, the chloride ion loses an electron and is oxidized.

Area 5 References

5R-1. An aid in the construction of titration graphs. Journal of Chemical Education, v. 26, No. 4: 188-191. April 1949

5R-2. Quantitative analysis. The Science Teacher, v. 27, No. 3: 37-40. April 1960

NOTES

Nuclear Energy

6.01. Sources of Information

Chemistry textbooks may not yet be adequate to guide all phases of this topic. One of the best basic references for teachers and pupils is *Sourcebook on Atomic Energy* by Samuel Glasstone, second edition, 1958. This book, prepared under the direction of the Atomic Energy Commission, is published and distributed by D. Van Nostrand Company, Inc. Also available as background material on the subject of radiation is *Teaching with Radioisotopes* which may be obtained from the Superintendent of Documents, United States Government Printing Office, Washington 25, D.C., for 40¢. The *Physics Handbook* and *Nuclear Survival*, published by the Department, contain other appropriate activities. Excellent articles are available in well-known encyclopedias. Detailed descriptions of the operation of Geiger counters and associated demonstrations may be found in the instruction manuals accompanying the commercially produced instruments. Additional references are furnished in the bibliography.

The following references found at the end of this unit may be useful in assigning to pupils specific topics outlined in the syllabus:

(1) Accelerators (*6R-1*)
(2) Nuclear reactors (*6R-2-3-4*)
(3) Radioisotopes (*6R-5-6*)
(4) Fission and fusion (*6R-7*)
(5) Civil Defense (*6R-8*)

6.02. Radiation Safety

The hazards of working with radioactive substances are designated as *internal* or *external*. Internal hazards involve the substance entering the body usually by way of the mouth; external hazards include exposure of the body to radiations from these substances. When the radioactive substances are in stoppered containers, the major hazard is from gamma radiation.

The amount of radioactive material normally available to high schools is controlled by Federal regulations. Provided that sensible procedures are used, there is little danger involved in working with these small amounts. The same types of procedures must be used as are used in industry where larger amounts are available and greater danger exists. See appendix *G-3* for further information on exposure permitted.

The following rules of laboratory procedure for teachers and pupils should be established and enforced when working with radioisotopes. In event that more stringent procedures are mandated by local, State or Federal regulations, the more stringent procedures should be followed.

- *NO* eating, drinking, smoking or using of cosmetics should be allowed in the laboratory. The ingestion of long-lived isotopes is particularly serious.
- *NEVER* pipette radioactive solutions by mouth.
- Wear rubber gloves and use tongs in moving containers.
- Use the fume hood if materials are to be ground or if vaporization may occur.
- Wash the hands after working with the materials.
- Monitor the hands, clothing and demonstration area with the Geiger counter after completion of cleanup operations.
- Treat radioactive materials as strong acids and keep them covered whenever possible.
- Open bottles carefully to prevent spilling.
- Treat all spills with large quantities of water and many rinses.
- Work with unsealed radioisotopes in plastic or steel trays lined with blotters or paper towels.
- Keep radioactive materials in a separate locked cabinet. Label them neatly by name and date of acquisition. If large amounts are stored, line the cabinet with sheet lead obtained from a plumber's supply house.
- Store glassware used with radioisotopes separately.
- Protect the detection apparatus from contamination by a single layer of material similar to Saran Wrap. The sensitivity will be only slightly decreased.
- Dispose of microcurie amounts of radioisotopes by diluting and flushing down the drain with large quantities of water.
- Account for all radioactive materials received, used, disposed of or stored.

6.03. Sources of Radioisotopes

Small quantities of radioisotopes may be available from local scientific supply houses or from hospitals in metropolitan areas. Inquiries at hospitals or to members of scientific societies may aid in locating a nearby source.

A partial list of suppliers of application-exempt quantities of iodine-131, phosphorus-32 and carbon-14 appears in appendix *G*. Contact the source of supply for information on quantities that may be purchased, price, method of shipment, special safety precautions, expected time of arrival and time to place order to ensure arrival on a specific date. Since most available radioisotopes have a short half-life, the activities should be performed soon after arrival of the shipment. Before ordering, check the school calendar and select as an arrival date one on which classes will not be eliminated or shortened. It is desirable to schedule two "clear" days in event of the late arrival of the shipment.

The following are examples of radioactive materials which can be used as sources of alpha particles, beta particles and gamma rays:

- *Alpha source*—usually obtainable by this name from scientific supply houses
- *Beta source*—phosphorus-32 (usual form $\mathrm{NaH_2P^*O_4}$), half-life of 14.3 days
- *Beta and gamma sources*—iodine-131 (usual form $\mathrm{NaI^*}$), half-life of 8.08 days *or* iron-59 (usual form $\mathrm{Fe^*Cl_3}$), half-life of 45.1 days

Note: The asterisk indicates the radioactive atom in the compound.

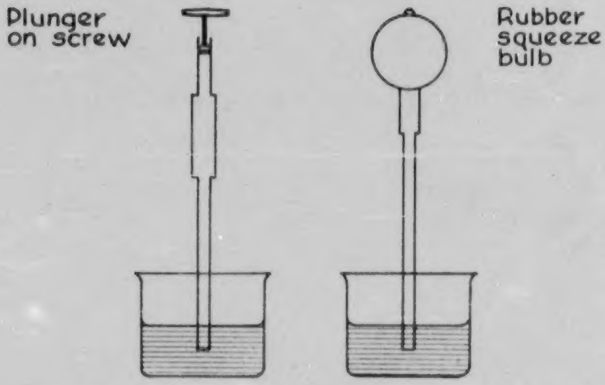
6.04. Handling of Unsealed Radioisotopes

Radioisotopes may be obtained in two forms, sealed and unsealed sources. The latter form is used for experiments involving chemical reactions. The unsealed source is in a vial in either powder or liquid form. The vial containing the usual quantity (10 microcuries) may appear to be empty upon receipt. However, the vial contains billions of radioactive atoms.

Monitor the container before unpacking. Unscrew the cap carefully to avoid spilling the material. If the radioisotope is dry and is to be used in solution, add a small quantity of distilled water to the vial to dissolve the material. Pour the liquid into a volumetric container. Wash the vial about five times with 4 to 5 ml. of distilled water from a wash bottle. Empty the vial each time into the volumetric container. After these rinses relatively few radioactive atoms remain in the vial.

Dilute the radioactive solution to the desired volume with distilled water. The concentration can be expressed in microcuries per milliliter of solution (uc/ml.).

See activity 6.02 for additional instructions for handling radioactive substances. Obtain measured amounts of the solution by use of a pipette. *CAUTION: Under NO circumstances should radioactive substances be pipetted by mouth. Do not use the "spit trap" method.* Create the partial vacuum necessary to enable the solution to rise by means of a squeeze bulb or similar device (see diagram 6.04). See the bibliography for additional details.

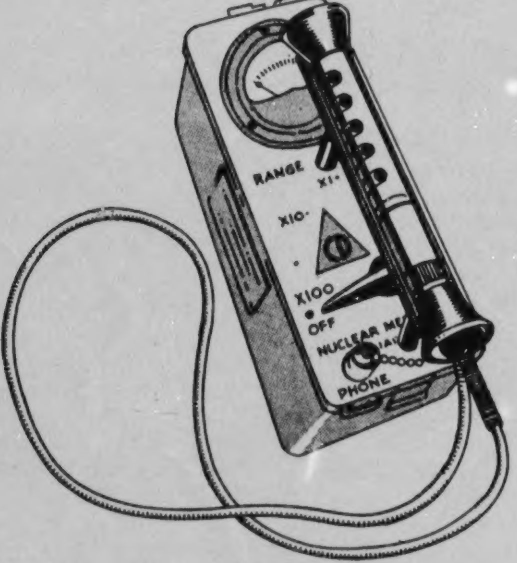


6.04

6.05. The Geiger Counter

A reasonable minimum of *qualitative* measurements may be made with many commercial Geiger counters or with the CD V-700 Radiological Survey Meter, Geiger Counter, Beta-Gamma Discriminating, 0-50 mr./hr. (see diagram 6.05). The latter instrument, distributed to all secondary schools in 1958-59 through the Office of Civil and Defense Mobilization, is suitable mainly for locating radioactive sources and monitoring clothing and hands. Reasonably accurate quantitative work requires the use of a count-rate meter which may be purchased from various supply houses. The manual accompanying each instrument is the best source of information for instructions on operating the particular instrument.

The following activities illustrate the correct use of some Geiger counters, their limitations, sources of error and proper interpretation of results. Consult the instruction manual for more complete details.



6.05

Excellent advanced mathematical interpretations are available in the bibliography.

a. **Operating Plateau of Variable Voltage Geiger Counters.** Determine the operating plateau for the tube according to instructions in the manual. This is the range of operating voltage for which the count rate is essentially constant. Operate the instrument at this voltage for further demonstrations.

Note: The CD V-700 Radiological Survey Meter has a *constant* voltage.

b. **Background Count.** Remove all known sources of radiation from the range of the counter. Record the counts each 10 seconds for 5 to 10 minutes. Average the results. Determine the average counts per minute. Subtract this average from all future readings. The background count is due to natural radioactivity, probably cosmic rays. See activity 6.06.

c. **Dead Time and Coincidence Loss.** Place a source *A* at a certain distance from the tube; record the count. Remove source *A* and replace with source *B*; record the count. Place sources *A* and *B* together; record the count. Note that the count rate for both sources together is less than the sum of the count rates for the individual sources. The instrument requires a certain time to "recover" from one count; in the meantime it "misses" some counts.

d. Other Factors Affecting Count Rate. In order to compare observations made with the Geiger counter, each observation must be made with the sample in the same relative position with respect to the counter. This arrangement is known as the geometry of the system. Many factors control the count rate, including the following:

(1) Distance from the source. If the source of radiation is fairly concentrated, the count rate varies inversely as the square of the distance from the source. For instance, at a distance of 6 cm. from the source, the count rate is ¼ the rate at 3 cm. from the source.

(2) Size of the window in the tube. Radiations from a source are emitted in all directions. If a complete count of all radiations at a point 3.0 cm. from a source were desired, it would be necessary to move the window of the tube along the entire area of the surface of an imaginary sphere with a radius of 3.0 cm. The surface area of this sphere is $4\pi r^2$ or 36πcm.^{2} (approximately 110 cm.^{2}). The area of the window of the tube is approximately 2 cm^2. Therefore, if the tube were held 3.0 cm. from the source, the counter in this position would register only 2/110 (approximately 2 percent) of the total counts provided that the efficiency of the tube were 100 percent.

(3) Scattering. Some radiations which are not traveling initially toward the window of the tube may be reflected from some nearby substances and pass through the window. This effect would increase the count rate. If the geometry of the system is identical for each observation, the proportion of radiations scattered may be assumed to be constant.

(4) Self-absorption. Some radiations (particularly low-energy beta particles) emitted from within a "thick" sample or a solution may be absorbed within the sample or solution. This self-absorption decreases the count. Generally, liquids containing radioactive materials must be almost completely evaporated by use of a heat lamp before counting is done. Sometimes the solution concentrated by evaporation is placed into a bottle cap planchet before the observation is made. The evaporation of most of the liquid decreases self-absorption.

e. Difference in Counting Between Beta and Gamma Rays. Particularly for low count rates, the Geiger counter is almost 100 percent efficient in counting beta rays. The efficiency in counting gamma rays is only about 2 percent.

6.06. Statistical Nature of Counting

Most measurements of nuclear phenonema are statistical in nature.

The determination of the random nature of cosmic ray observations in activity 6.05*b* is a partial illustration.

Assume that the number of counts for each of sixty 5-second intervals was recorded by a series of tallies after the numbers representing the number of counts per interval. The tally sheet might appear as follows:

Counts/Interval	Intervals	Counts/Interval	Intervals
0	/	5	////
1	𝍸 /	6	//
2	𝍸 𝍸 ///	7	//
3	𝍸 𝍸 𝍸 //	8	/
4	𝍸 𝍸 ///	9	/

For instance, according to this tally sheet, there were six intervals during which only one count was recorded. The most probable number of counts per interval is three. The total number of counts recorded is the sum of the individual products of counts/interval and interval. By dividing the total number of counts (198) by the number of 5-second intervals (60), one obtains the average number of counts per interval. In this case, it is 3.3. This corresponds to about 40 counts per minute.

Then, to illustrate that reliability is only obtained in such measurements by use of a large enough data sample, the number of pulses in a minute can actually be counted several times. It is seen that these results are much more consistent than the counts obtained in the small 5-second intervals.

6.07. Locating Radioactive Substances

Pupils are usually interested in locating sources of radioactivity by use of the Geiger counter. For variation, hide some samples and locate them with the instrument. Positive results may be obtained by monitoring the following.

a. Luminous Paint. This paint is usually of two types. One type contains a phosphorescent material, requires strong light to be luminous and is not radioactive. The other contains a trace of radium (about one microcurie) plus a fluorescent material and does not depend upon exposure to light. The latter type is used on many watches and clocks as well as the instrument dials on some surplus equipment. Large clocks may have a 3—5 microcurie source. Remove the face glass to allow more beta particles to reach the detector. Improved performance results if some material is scraped from the clock, placed in a porcelain crucible and heated to red heat for several minutes to burn out organic binders. *CAUTION: Use the hood.*

b. **Glazes.** Bright orange and black glazes for pottery may contain oxides of uranium. Some types of laboratory spot plates and crucibles are finished in this black glaze (strength about 2 x 10^{-3} microcuries/cm.^{2}) to make small traces of white precipitates more visible. Orange plates and cups are possible sources.

c. **Glasses.** Glass of a pale yellow-green hue ("uranium glass") used for Geissler tubes found in the physics laboratory is a good source.

d. **Radioactive Ores.** Pitchblende, carnotite and monazite sand (contains thorium) may be used. They are obtained from scientific supply houses.

e. **School Rock Collection.** Local rocks are possible sources.

f. **Gas Mantles.** Portable camp lanterns (available at hardware stores at low cost) may be used. They contain crude lanthanide oxides (nonradioactive) contaminated with thorium (radioactive).

g. **Uranium Compounds.** These may be purchased from scientific supply houses without special license. Uranyl nitrate, $UO_2(NO_3)_2 \cdot 6H_2O$, and uranyl zinc acetate are water-soluble and cost about $3 per ounce.

h. **Radioactive Standards.** These are used to calibrate detection instruments and are available in scientific supply houses.

6.08. Calibrating Radioactive Sources

a. The strength of a radioactive source decreases with time. For instance, I^{131} has a half-life of about 8 days. A 10-uc. sample of I^{131} will be 5 uc. in 8 days, 2.5 uc. in 16 days and so on. It is often necessary to compute the level of radioactivity of a radioactive sample each time it is used. This is especially true when the half-life of the isotope is very short.

The following table will simplify calculations of new strength or original strength for any isotope with a known half-life.

Some sample calculations making use of the table are given below:

(1) *The half-life of Na^{24} is 15 hours. What will be the activity of a 10.0-uc. sample of Na^{24} after 6 hours?*
6 hours = 6/15 half-life = 0.4 half-life
The table indicates 75.9 percent will remain after 0.4 half-life.
In 6 hours, the activity will be 0.759 x 10.0 uc. or 7.59 uc.

(2) *A sample of Na^{24} has a count rate of 1,000 counts per minute at noon. Under the same conditions what would its count rate have been at 9:00 a.m.?*

Time Expressed as Fraction of Half-Life	Fraction of Original Activity Remaining	Reciprocal Activity
0.05	0.965	1.035
0.10	0.933	1.072
0.15	0.900	1.109
0.20	0.870	1.149
0.25	0.841	1.188
0.30	0.811	1.231
0.35	0.784	1.275
0.40	0.759	1.318
0.45	0.732	1.365
0.50	0.706	1.415
0.55	0.684	1.464
0.60	0.660	1.515
0.65	0.637	1.570
0.70	0.616	1.624
0.75	0.595	1.682
0.80	0.574	1.741
0.85	0.554	1.802
0.90	0.535	1.866
0.95	0.516	1.933
1.00	0.500	2.000
1.2	0.435	2.298
1.4	0.379	2.641
1.6	0.330	3.034
1.8	0.287	3.890
2.0	0.250	4.000
3.0	0.125	8.000
4.0	0.062	16.000

Time is 3 hours = 3/15 half-life = 0.2 half-life.

The reciprocal for 0.2 half-life is 1.149.

The count at 9:00 a.m. would have been 1.149 x 1,000 counts/min. or 1,149 counts/min.

b. The following table for I^{131} *only* gives the approximate percentage *remaining* up to 32 days after calibration. The calculations are based on the approximate half-life of 8.0 days for I^{131}.

IODINE-131 DECAY CHART

Hours	Percentage Remaining	Days	Percentage Remaining
1	99.6	1	91.7
2	99.3	2	84.1
3	99.0	3	77.1
4	98.6	4	70.7
5	98.2	5	64.9
6	97.9	6	59.4
7	97.5	7	54.6
8	97.2	8	50.0
9	96.8	9	45.9
10	96.5	10	42.1
11	96.1	11	38.6
12	95.8	12	35.3
13	95.4	13	32.5
14	95.1	14	29.8
15	94.7	15	27.3
16	94.3	16	25.0
17	94.0	17	23.0
18	93.7	18	21.0
19	93.4	19	19.3
20	93.0	20	17.7
21	92.7	21	16.2
22	92.4	22	14.9
23	92.0	23	13.7
24	91.7	24	12.5
		25	11.5
		26	10.5
		27	9.6
		28	8.9
		29	8.1
		30	7.4
		31	6.8
		32	6.3

A sample calculation using this table is shown.

A sample of I^{131} calibrated at 10.0 uc. for 9:00 a.m. Monday cannot be used at that time because the school has been closed. What will be the strength at 9:00 a.m. Wednesday?

$$0.841 \times 10.0 \text{ uc.} = 8.41 \text{ uc.}$$

6.09. Separating Emanations

Positive alpha particles, negative beta particles and gamma rays (no charge) may be separated by passing them between charged plates. The alpha particles tend to move toward the negative plate, the beta particles tend to move toward the positive plate; the gamma rays are unaffected. Details are found in physics texts and the *Physics Handbook*.

These emanations may also be separated on the basis of their penetrating power. *Note:* Demonstration 6.09*a* may not give satisfactory results with all electroscopes.

a. Charge a simple foil leaf electroscope. Note the rate at which it discharges. Recharge the electroscope. Bring a known alpha source near the knob. Note that the rate of discharge increases.

Bring the same alpha source near the Geiger tube with the shield open. No noticeable change occurs in the count rate since alpha particles cannot penetrate the walls of the usual Geiger tube.

b. Bring a known beta-gamma source near the Geiger tube with the shield open. Record the count rate. Close the shield and record the count rate. The difference in count rate is due to the beta radiation which cannot penetrate the shield. Only about one percent of the gamma radiation passing through the tube causes impulses. Therefore, the count rate recorded for a gamma source represents only a small percentage of the actual gamma radiation.

6.10. Effect of Chemical Change on Radioactivity

One of the most basic concepts in introductory nuclear chemistry is the effect, *if any*, of chemical change on radioactive substances.

a. To each of two 50-ml. Erlenmeyer flasks add 5 ml. of 2N NaI solution. Monitor each container to show that it is free of radioactivity. To one flask add 5 microcuries of radioactive I^{131} in a solution of NaI^*. Check the radioactive solution with the Geiger counter. Prepare a saturated solution of $Pb(NO_3)_2$ and show that it is free from radioactivity.

Add 20 ml. of saturated $Pb(NO_3)_2$ solution to each flask. Mix thoroughly, using glass rods, and let the contents settle for 20 minutes. Test the supernatant liquid with one drop of $Pb(NO_3)_2$ solution to see if the reaction has been completed. After complete precipitation and settling, decant the liquid in each container through filter paper into separate containers. Test each precipitate and filtrate with the Geiger counter. Each yellow precipitate appears the same. However, the radioactive I^{131} in the original NaI^* solution has now become associated with the precipitate of PbI_2. *Note:* The solubility product constant (K_{sp}) of PbI_2 at 25°C. is 1.39 x 10^{-8}. Actually a small amount of I^{*-} is present but may not be detected by the Geiger counter (relate to activity 9.08).

b. Radioactive Fe^{59} has a half-life of 45.1 days and therefore has a longer "shelf life" than either I^{131} or P^{32}. If more convenient, follow the same procedures as in activity 6.10*a*, but use $FeCl_3$ solution, radioactive Fe^{59} in a solution of Fe^*Cl_3, and NaOH. The precipitate will be $Fe(OH)_3$ containing some $Fe^*(OH)_3$. *Note:* Only 1 uc. of Fe^{59} may be obtained unsealed.

c. Place 5 uc. of radioactive I^{131} in NaI^* solution in a pill bottle. Cap the bottle with a polyethylene snap lid. Check the counts per minute with the Geiger counter.

Place into a 250-ml. beaker 5 ml. of 2N NaI solution and the 5 uc. of the I^{131} solution (NaI^*). Add 1 gm. of MnO_2 and 10 ml. of concentrated H_2SO_4. Cover the beaker with an evaporating dish half full of cool water. *CAUTION: Use the hood.* Heat the beaker gently until the violet color disappears. Let the container cool. Note that this is an adaptation of the laboratory preparation of iodine illustrated in diagram 4.37*a*.

Wash the pill bottle and check for background count. Scrape the crystals of iodine from the underside of the evaporating dish into the pill bottle. Do not touch the iodine crystals with the fingers. Cap the bottle and check with the Geiger counter. Note that I^{131} is radioactive whether combined in NaI or free. The chemical change involved the outer electrons only and not the nuclei of the radioisotope. In this reaction, all the iodide may not have been oxidized or some free iodine may remain on the sides of the beaker. Monitor the reactants or the beaker if this condition is to be illustrated.

6.11. Radioautographs

Place a coleus cutting in a solution containing 10 uc. of phosphorus-32 for about 2 to 4 days. After a significant increase in beta radiation is detected in the leaves, by use of a Geiger counter, a radioautograph may be made. Wrap the leaves with a single layer of Saran Wrap. Lay the leaves on X-ray film in a film holder. Expose overnight and develop the film. As experimentation will indicate, the necessary time of exposure increases as the strength of the radioisotope in the leaves decreases.

6.12. Equations of Nuclear Reactions

Nuclear reactions resulting from particles entering or leaving the nucleus may be represented on a felt board or on an overhead projector with the aid of plastic cutouts. Refer pupils to some form of the periodic table to enable them to follow the changes that occur.

The *Reference Tables for Chemistry* should be available to pupils. Pupils will be expected to complete and balance many types of equations of nuclear reactions with the aid of information on the second and third pages of the tables (see pages 334-335). Pertinent portions are "Periodic Table of the Elements" and "Symbols of Some Particles." In addition, the following rules will be of considerable assistance:

(1) Alpha particle emission results in a new element with the atomic number decreased by *two* and the mass number decreased by *four*.

(2) Negative beta particle emission results in a new element with the atomic number increased by *one*.

(3) On each side of the equation the sum of the atomic numbers (or charges in cases such as beta emission) is the same.

(4) On each side of the equation the sum of the mass numbers is the same.

Following are illustrative examples of equations of nuclear reactions which need not be memorized but which can be written using the reference sources and rules cited above. The explanation of the reasoning is included for some examples.

PROBLEM: *Write the equation for alpha emission by radium*^{226}.
ANSWER: ${}_{88}Ra^{226} \rightarrow {}_{2}He^{4} + {}_{86}Rn^{222}$
EXPLANATION: ${}_{88}Ra^{226}$ (See periodic table for atomic number and mass)
${}_{2}He^{4}$ (See "Symbols of Some Particles")
86 (See rules *1* and *3*)
Rn (See periodic table for atomic number 86)
222 (See rules *1* and *4*)

PROBLEM: *Write the equation for beta emission of lead-210.*
ANSWER: ${}_{82}Pb^{210} \rightarrow {}_{-1}e^{0} + {}_{83}Bi^{210}$
EXPLANATION: Lead (See periodic table for atomic number and mass)
Beta particle (See "Symbols of Some Particles")
Atomic number 83 (See rules *2* and *3*)
Bi (See periodic table for atomic number 83)

PROBLEM: *Nitrogen may be transmuted by bombardment with alpha particles. Complete the equation:*
${}_{7}N^{14} + {}_{2}He^{4} \rightarrow {}_{8}O^{17}$ + some particle

ANSWER: $_7N^{14} + {}_2He^4 \rightarrow {}_8O^{17} + {}_1H^1$

EXPLANATION: Atomic number 1 (See rule *3*)
Mass number 1 (See rule *4*)
H (See periodic table for atomic number 1)

PROBLEM: *Complete the following equation:*
alpha particle + beryllium^9 → carbon^{12} + some particle.

ANSWER: $_2He^4 + {}_4Be^9 \rightarrow {}_6C^{12} + {}_0n^1$

6.13. Determination of Half-Life

a. Graphing. A rough approximation of the half-life of a short-lived radioisotope is possible as a teacher demonstration. Place the probe of the Geiger counter at some convenient distance for a source so that the count rate is high but on scale. Disregard the background count since it introduces a very small error. Record the count rate and time of observation. Repeat this procedure at convenient intervals for slightly more time than the known half-life of the source. Each time keep the probe *the same distance* from the source.

Plot these data on graph paper with time represented on the abscissa and counts per minute represented on the ordinate.

Draw a smooth curve through or near the points. If the count rate is high, use semilog paper with counts per minute plotted on the ordinate. In this case the curve is essentially a straight line.

Determine the point on the curve where the counts per minute is one-half the initial reading. The corresponding time is the half-life.

b. Mathematical Applications.

(1) Graph the equation, $y = 2^{-x} = \frac{1}{2^x}$. This curve is similar to the actual half-life curve.
When $x = 0$, $y = 1$; when $x = 1$, $y = \frac{1}{2}$ and so on.

(2) One form of the equation of exponential decay is $A_n = \frac{A_0}{2^n}$ where A_0 is the original activity, n is the number of half-life intervals, and A_n is the activity after n half-life intervals. The half-life of Na^{24} is 15 hours. Compute the activity of 10 uc. of Na^{24} after 30 hours.
$n = 2$ half-lives

$A_n = \frac{10\text{ uc.}}{2^2} = 2.5$ uc. (Compare with the results obtained by using the table in activity 6.08*a*.)

(3) Another form of the equation of exponential decay is $M_n = \frac{M_0}{2^n}$ where M_0 is the original mass.

The half-life of ruthenium-106 is 1.0 years. How much Ru^{106} remains of an original 80-gm. sample of Ru^{106} after 4.0 years?

n = 4 half-lives

$$M_n = \frac{80 \text{ gm.}}{2^4} = \frac{80 \text{ gm.}}{16} = 5.0 \text{ gm.}$$

(4) The half-life of thallium-204 is 1.0 years. A sample of Tl^{204} weighs 10 gm. What was the probable weight of the Tl^{204} two years ago?

n = 2 half-lives

$$10 \text{ gm.} = \frac{M_0}{2^2}$$

$$M_0 = 40 \text{ gm.}$$

c. *Advanced Mathematical Application.*

If pupils are adept at handling mathematics, a more quantitative treatment is possible.

One form of the equation for exponential decay is

$N = N_0 e^{-.693t/t_{1/2}}$ where N_0 = initial count rate
N = count rate at a later time
t = time between readings
$t_{1/2}$ = half-life.

$$\ln N = \ln N_0 - .693 \frac{t}{t_{1/2}}$$

$$\text{In } N - \text{In } N_0 = .693 \frac{t}{t_{1/2}}$$

Note: ln is the natural logarithm.

$$t_{1/2} = \frac{-.693t}{\ln N - \ln N_0}$$

The actual data recorded in an experiment with I^{131} were:

N_0 = 5,900 counts per minute
N = 3,500 counts per minute
t = 168 hours (one week)

Using these data and the equation above compute Bthe half-life of I^{131}.

The calculations follow:

$$t_{1/2} = \frac{-(.693)\ (168)}{\ln 3{,}500 - \ln 5{,}900} = \frac{-116}{\ln \frac{3{,}500}{5.900}}$$

$$= \frac{-116}{\ln .594} = \frac{-116}{-.521} = 223 \text{ hours.}$$

By using 193 hours as the accepted half-life for I^{131} the percentage of error for this example is $\frac{223-193.}{193} = 15.5$ percent. This error is due largely to failure to correct for resolution ("dead time"). Note also that, if a lower count rate had been used, the background count would have been significant. For details on these corrections see *Teaching with Radioisotopes*, particularly the discussion of "The Mathematics of Exponential Decay" and the two experiments that follow.

6.14. Equivalence of Mass and Energy

Teachers may wish to use the Einstein equation to illustrate the equivalence of mass and energy as it applies to various chemical and nuclear reactions.

a. According to the law of conservation of mass, mass is conserved in ordinary chemical reactions. However, the Einstein equation indicates that, if heat and energy is evolved, some mass must have been lost. To illustrate why this loss of mass has not been detected, compute the loss of mass involved in burning 100.0 gm. of hydrogen in oxygen to form water vapor. The heat released is about 2,867,000 calories or about 12,000,000 joules (1 calorie = 4.18 joules.)

The Einstein equation is:

$E = mc^2$ where E may be expressed in joules, m in kilograms and c (the velocity of light) in meters/second.

$$\begin{aligned} \text{m (kilograms)} &= \frac{12 \times 10^6 \text{ joules}}{(3.0 \times 10^8 \text{ m./sec.})^2} \\ &= 1.3 \times 10^{-10} \text{ kilograms.} \\ \text{or } &\ 1.3 \times 10^{-7} \text{ grams.} \end{aligned}$$

The result indicates that approximately 1.3×10^{-7} gm. of mass were converted to energy when about 900 gm. of water vapor were formed. This represents a loss of about 13 parts per billion which cannot be detected by the most sensitive balance we have today.

b. Calculate the loss in mass during a nuclear reaction which liberates energy equivalent to that from the explosion of one million tons of T.N.T. The heat of combustion of T.N.T. is 3,613 calories per gram.

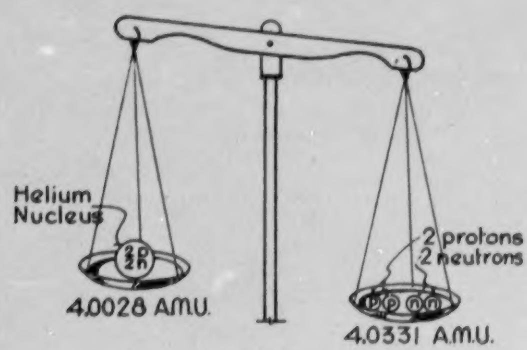
$$\begin{aligned} \text{Mass of T.N.T.} &= 10^6 \text{ tons} \times 9.07 \times 10^5 \frac{\text{gm.}}{\text{tons}} \\ &= 9.07 \times 10^{11} \text{ gm.} \end{aligned}$$

$$\begin{aligned} \text{Energy from T.N.T.} &= 9.07 \times 10^{11} \text{ gm.} \times 3.61 \times 10^3 \frac{\text{calories}}{\text{gm.}} \\ &= 3.27 \times 10^{15} \text{ calories} \\ &= 1.37 \times 10^{16} \text{ joules (since 4.18 joules = 1 calorie)} \end{aligned}$$

From activity 6.14a

$$\begin{aligned} m(\text{kg.}) &= \frac{1.37 \times 10^{16}\ \text{joules}}{(3.00 \times 10^{8}\ \text{m./sec.})^{2}} \\ &= \frac{1.37 \times 10^{16}}{9.00 \times 10^{16}} \\ &= .151\ \text{kg.} \end{aligned}$$

or 151 grams.



6.14

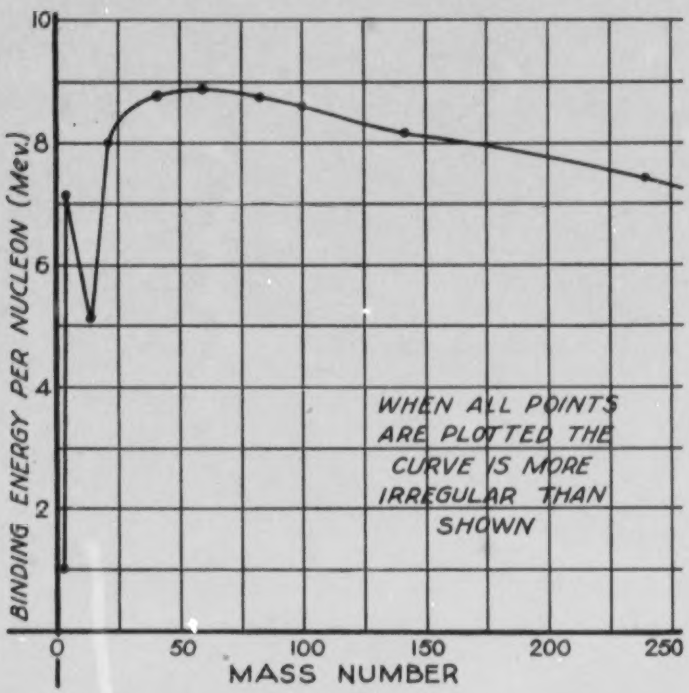
6.15. Binding Energy

Confusion sometimes arises when the term binding energy is introduced into a discussion of nuclear reactions. Care must be taken to be sure the pupils understand the difference between force and energy. Point out that "binding energy" is not a force but the work that would be required to separate a nucleus into individual nucleons. When using the term binding energy, it is also necessary to distinguish "binding energy per nucleus" from "binding energy per nucleon." Point out the difference to the pupils.

From empirical data (such as mass spectrograph measurements) we know that the mass of any atomic nucleus is always less than the sum of the masses of protons and neutrons composing it. This difference, or loss, in mass of the nucleus is called the *mass defect.* By use of Einstein's equation, $E = mc^2$, it is possible to calculate how much energy is equivalent to any particular mass defect. When this mass defect is stated in terms of its equivalent energy (one atomic mass unit = 931 million electron volts), it is called the *binding energy.* When any nucleus was originally formed from neutrons and protons, the energy released was equal in amount to the mass defect.

A rough analogy can be made to the release of energy (heat) when hydrogen and fluorine combine. Therefore, one should think of binding energy as energy which *has been* released, *not* as energy possessed by the nucleus. To carry the analogy further, when hydrogen fluoride is separated into the elements, hydrogen and fluorine, energy is required from outside. This is also true in the case of a nuclear reaction. In order to "break up" a nucleus into its constituent particles, the energy formerly released must be returned. This energy is referred to as "binding energy."

In order to explain fission and fusion reactions, it is necessary to use the *binding energy per nucleon.* Because of the geometrical configurations of the nucleons within a nucleus, the binding energy per nucleon varies from atom to atom (see diagram 6.15).



6.15

Following is a table showing the calculations for the binding energy per nucleon for some isotopes. Results will vary slightly depending upon the reference sources.

ISOTOPE	MASS (A.M.U.)	MASS OF INDIVIDUAL PARTICLES (A.M.U.)	MASS DEFECT (A.M.U.)	MASS DEFECT PER NUCLEON (A.M.U.)	BINDING ENERGY PER NUCLEON (MEV.)*
Proton	1.0081				
Neutron	1.0090				
${}_{1}H^{2}$	2.0147	2.0171	.0024	.0012	1.12
${}_{2}He^{4}$	4.0039	4.0342	.0303	.0076	7.08
${}_{3}Li^{6}$	6.0169	6.0513	.0344	.0057	5.31
${}_{3}Li^{7}$	7.0182	7.0603	.0421	.0060	5.59
${}_{4}Be^{9}$	9.0151	9.0774	.0623	.0069	6.42
${}_{10}Ne^{20}$	19.9987	20.1709	.1722	.0086	8.01
${}_{20}Ca^{40}$	39.9753	40.3418	.3665	.0092	8.57
${}_{26}Fe^{56}$	55.9533	56.4812	.5279	.0094	8.75
${}_{36}Kr^{84}$	83.939	84.723	.784	.0093	8.66
${}_{42}Mo^{100}$	99.939	100.861	.922	.0092	8.56
${}_{57}La^{139}$	138.955	140.198	1.243	.0089	8.29
${}_{92}U^{238}$	238.125	240.056	1.931	.0081	7.54

* 1 a.m.u. = 931 million electron volts (Mev.).

The nuclei of the lightest and heaviest elements have relatively low binding energies per nucleon, while the nuclei of those elements near the center of the periodic chart (iron and so on) have the greatest binding energy per nucleon. This means that iron has a more stable nucleus than helium or lead. *Note:* The *total* binding energy in a nucleus of lead is greater than the *total* binding energy in a nucleus of iron, even though the binding energy *per nucleon* is less in lead.

The release of energy by both fission of heavy elements and by fusion of light elements is explained by using the concept of binding energy per nucleon. When two light nuclei fuse into a heavier nucleus, a more stable configuration of nucleons is reached. The binding energy per nucleon is greater, because this difference in energy has been released. (Binding energy is the energy *released* when nuclei form a more stable configuration.) When a heavy element fissions, the newly created elements also have more stable configuration. The binding energy per nucleon is again greater, because this difference in energy has been released.

In nuclear reactions then, the mass converted to energy is not due to the annihilation of any particle. It is due to the loss in mass of each nucleon as it is rearranged to form a more stable nucleus.

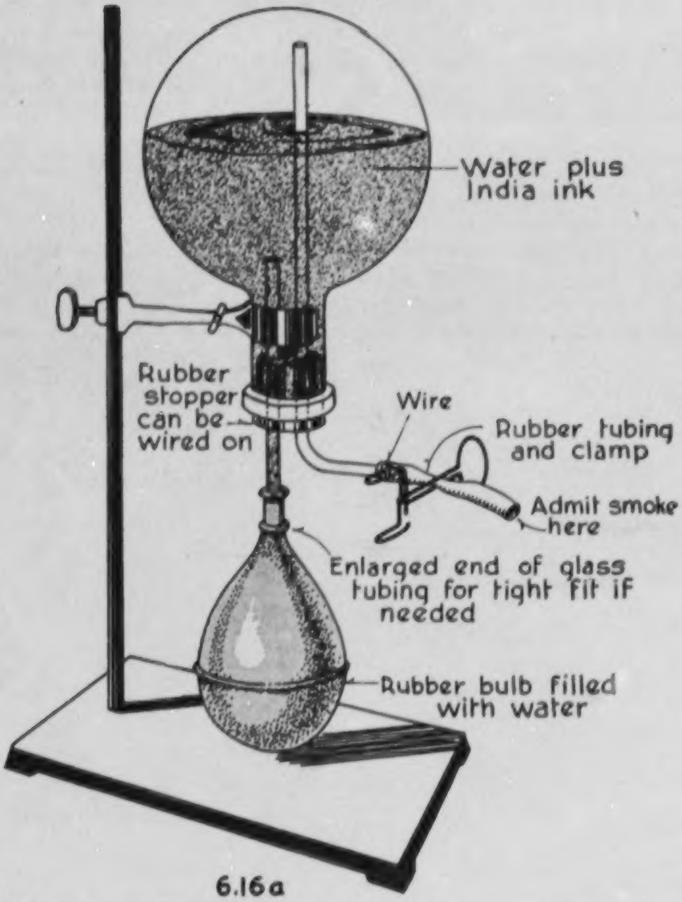
6.16. Cloud Chambers

The cloud chamber gives dramatic, visual evidence of radioactivity and readily stimulates class discussion. Cloud tracks due to radioactivity are most reliably demonstrated in a pulse-type chamber. Although diffusion chambers can be balky and do not make sure-fire demonstrations, they can be made in a few minutes from simple materials and are worth some patient experimentation.

a. Principle of Cloud Formation. The principle of cloud formation can be demonstrated without the use of a radioactive source. Use a commercial apparatus or set up a flask of any convenient size according to diagram 6.16*a*. Use a flask with a capacity three to four times that of the rubber bulb. Squeeze the bulb slowly to compress the air above the water and hold for several seconds to permit the heat of compression to dissipate. Release suddenly and a fog or cloud will form due to the cooling effect of an expanding gas. The air which was saturated with water vapor at room temperature is suddenly cooled and can no longer hold so much vapor. The excess precipitates out as minute droplets of water.

This procedure may be repeated many times, but eventually the air will become cleaned of dust particles and ions that act as nuclei for the precipitation process, and no cloud will form on expansion. Instead, the air momentarily retains all the water vapor in a supersaturated solution. To observe this effect, allow the apparatus to stand for a day or two. If some smoke particles from a match are admitted through the side tube, excellent cloud formation will again be noted. If the air admitted into the apparatus is filtered through a tube packed with dry cotton no cloud will form. Store the apparatus for future use. See also *Physics Handbook*, activities 2.37 and 6.19.

b. Pulse-Type Chambers. These cloud chambers operate on the principle described in activity 6.15*a*. Special precautions are taken to


Water plus India ink
Rubber stopper can be wired on
Wire
Rubber tubing and clamp
Admit smoke here
Enlarged end of glass tubing for tight fit if needed
Rubber bulb filled with water

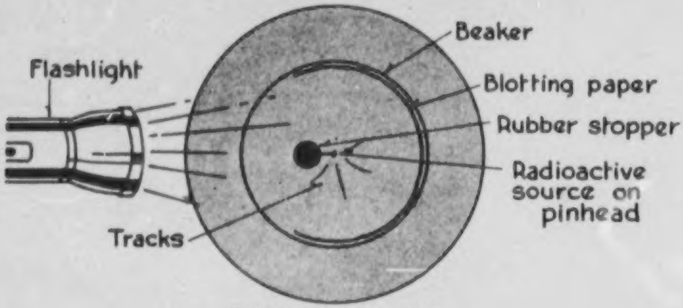
6.16a

exclude dust and ions, in order to create the supersaturated condition. If a cosmic, alpha, beta or gamma ray passes through the air, it will strip electrons from air molecules, leaving a trail of ions in its path along which water droplets will condense. The shape, length and density of the track depend upon the type of ray and its energy. If *a* above is operated just at the instant a cosmic ray passes through the apparatus, a track will be evident. Usually, a small amount of radioactive substance is inserted into the air space instead. Since dust particles normally bear a static charge, they and any unwanted ions are attracted to the sides by positive and negative plates.

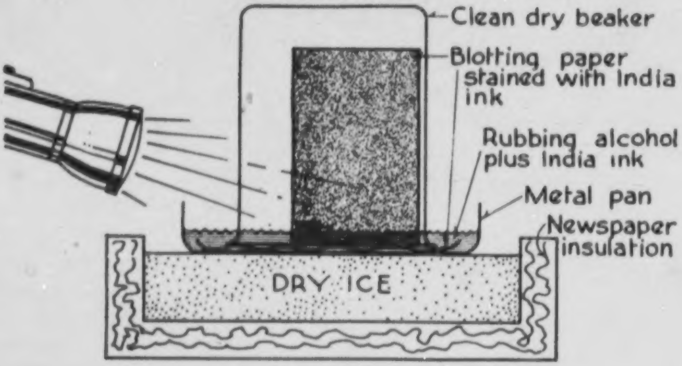
c. **Diffusion Types.** These chambers operate by allowing air saturated with alcohol vapors to sink to colder regions in dust-free air. In a certain region where supersaturation occurs, tracks will become visible. Unlike the pulse type, these tracks are constantly visible. Good commercial instruments are available, but interested pupils may wish to make their own chambers.

Place rubbing alcohol mixed with a few drops of India ink or indophenol in a shallow metal pan (see diagram 6.16c). (Any kind of alcohol or alcohol-water mixture is usable.)

Fasten an alpha source to a piece of cork. A small chip of radioactive luminous paint may be used if it has been heated red hot in a crucible, cooled and attached to a pin head with a thin film of clear cement. Place the source so that it remains about 1 cm. above the surface of the alcohol.


Beaker
Flashlight
Blotting paper
Rubber stopper
Radioactive source on pinhead
Tracks

OVERHEAD VIEW


Clean dry beaker
Blotting paper stained with India ink
Rubbing alcohol plus India ink
Metal pan
Newspaper insulation
DRY ICE

SIDE VIEW

6.16c

Stain a rectangle of blotting paper with India ink. Invert a clean, dry 400- or 500-ml. beaker with the blotting paper inside over the alcohol.

Place the metal pan on a block of dry ice. *CAUTION: DO NOT have any glass, wood or other insulators between the dry ice and the pan.* If "dry ice snow" made with commercial apparatus is used, mix the snow with a small amount of acetone. Allow the apparatus to cool 15 to 30 minutes until a temperature equilibrium is established.

Induce a static electric charge on a piece of sheet plastic by rubbing it with a cloth. Touch the plastic several times to the top of the beaker. This will clear the air space of unwanted ions.

Illuminate the side of the container with a spotlight or flashlight as shown. Observe the tracks near the source.

Area 6 References

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6R-3. Lost and gone forever. Journal of Chemical Education, v. 32, No. 5: 275. May 1955

6R-4. "Atoms for peace" moves along; AEC ticks off for Congress the status of its programs to help foreign nations use the atom peacefully. Chemical and Engineering News, v. 36, No. 33: 21-23. Aug. 1958

6R-5. Radioisotopes in industry. J. R. Bradford, ed. Reinhold

6R-6. The scope and future of isotope utilization. Journal of Chemical Education, v. 30, No. 5: 229-234. May 1953

6R-7. The discovery of fission. Scientific American, v. 198, No. 2: 76-84. Feb. 1958

6R-8. Atmospheric radioactivity studies at the U. S. Naval Research Laboratory. Journal of Chemical Education, v. 36, No. 6: 291. June 1959

6R-9. Radioactivity experiments for high schools using orange glazed ceramics. Journal of Chemical Education, v. 36, No. 4: 202-204. April 1959

NOTES

A [illegible]

AREA 7

Organic Chemistry

7.01. Introduction to Organic Chemistry

The topic of organic chemistry should be one of the most interesting and stimulating of the various areas taught in the high school chemistry course. The opportunity to bring the subject matter very close to the everyday lives of the pupils and to provide material which challenges the imagination and resourcefulness of virtually all pupils is quite apparent. Since the turn of the century no other field of knowledge has contributed more to the material welfare and economy of the Nation than has the field of chemistry; the major portion of this contribution has been in the area of organic chemistry.

The term "*organic*," as it is now used in its chemical sense, should be clearly defined and well understood by the pupils at the outset of the unit of study. In this connection, a discussion of the experimentation of Friedrich Wöhler (1828), in which he converted ammonium cyanate, a substance not of living origin, into urea, which had previously been associated only with living cells, will help to point out the need for broadening the definition of the term from its original meaning. During recent years the discovery and synthesis of compounds in which atoms of silicon assume a position in various compounds formerly occupied only by carbon atoms have further broadened the scope and variety of organic synthesis. Such compounds, commonly referred to as silicones, possess a number of unique properties which make them useful in a great diversity of commercial products, including, for example, waterproofing materials, waxes, nonreactive and high boiling point lubricants, and electrical insulators.

The subject of covalent bonding, which has been discussed earlier in the course, is particularly well illustrated as this area of organic chemistry is developed. Pupils will be impressed not only by a comparison of the relative numbers of organic and inorganic compounds (approximately 600,000 to 30,000), but also by the fact that virtually all new chemical compounds discovered can be classified as organic compounds (an average of at least 30,000 per year).

The questions of why there are so many organic compounds and why the number continues to grow so rapidly will make an excellent starting point for the teaching of organic chemistry. In such a discussion, review the principle of covalent bonding and point out the rather unique behavior of carbon atoms in sharing one, two or three electrons with other carbon atoms in virtually unlimited numbers and patterns. This preliminary discussion should focus primarily on the various types of hydrocarbon molecules. The substitution of other elements (such as the halogens) and functional groups (such as CH_3) for hydrogen contributes further to the endless variety of compounds.

Considerable attention and time will be devoted to the study of hydrocarbons in any discussion of organic chemistry, not only because there are a great many familiar and very useful compounds in this group, but also because many of the important fundamental principles involved in the formation of organic compounds are well illustrated by this group. Actually, all other types of organic compounds can be considered structurally as substituents of the hydrocarbon molecule. A complete class discussion of hydrocarbons is desirable at this point.

7.02. The Tetrahedral Carbon Atom

Establish the concept of the three-dimensional molecule at the outset of the discussion in this area; reemphasize continuously throughout the unit. Various commercial molecule building sets are available to illustrate this concept, many of which allow excellent spatial visualization (see appendix *B-2*).

Since these sets tend to be rather expensive, many teachers may prefer to build their own molecular models from the styrofoam spheres which are readily available. Water base paints can be used effectively in coloring these spheres either by dipping or spraying. The use of certain types of paints and lacquers is not advised because the styrofoam may be dissolved by some of the solvents used in such paints. Short pieces of quarter-inch dowel or plastic soda straws used to represent the bonds between various atoms will emphasize the fact that each bond actually represents a pair of shared electrons. Permanent molecular models can be prepared by cementing the dowels in place in the holes in which they are inserted into the spheres. A very satisfactory cement for this purpose can be prepared by dissolving styrofoam, which has been broken up into small pieces, in xylene using sufficient styrofoam to make a fairly viscous fluid. Since the methane molecule is fundamental to all subsequent discussion it would certainly be worthwhile to construct a fairly accurate representation of this molecule, particularly with respect to bond angles. *Note:* It is not advisable to spend large portions of class time in constructing models nor to require pupils to spend excessive time out of school in their production.

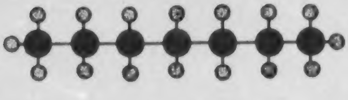
7.03. The Principle of Isomerism

Probably the simplest approach to this extremely important and fundamental concept is examining various possible structures of a molecule such as dichloromethane (CH_2Cl_2).

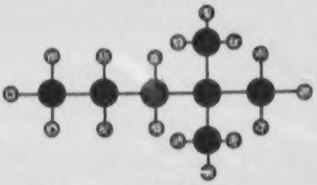
If the possibility of a two-dimensional molecule in the form of a square is accepted (as often diagramed on paper or on the blackboard), there will be only two possible structures for this molecule. Since these two structures are different from each other, they would represent isomers of this compound.

If molecular models of dichloromethane are constructed in the tetrahedral form, the two models, which at first appear quite different from each other, will be found to be identical when the position of one of the molecules is changed. Since only one isomer of dichloromethane has actually been identified, this illustration would support the concept of the tetrahedral arrangement. In this arrangement all the hydrogen atoms, or atoms substituted for them, are the same distance from each other.

Some common isomers are found among members of the paraffin (methane) series. In normal heptane (n-heptane) the seven carbon atoms are arranged in a chain with the 16 hydrogen atoms on either side of the carbon atoms and on the ends of the chain. In an isomer of heptane five carbon atoms are arranged in a chain while two other carbon atoms with attached hydrogen atoms (methyl groups) branch from the chain. The structural nomenclature, 2, 2-dimethylpentane, indicates that two methyl groups (CH_3) are located on the second carbon atom from the right (as shown below). See references *7R-1-2*.



n-heptane



Isomer of heptane
2,2-Dimethylpentane

7.04. Preparation of Methane

TEACHER DEMONSTRATION ONLY: Using a setup identical to that for the laboratory preparation of oxygen by heating a chlorate, mix 5 gm. of anhydrous sodium acetate and 10 gm. of soda lime (mixture of calcium oxide and sodium hydroxide) in a large pyrex test tube. Heat this mixture and collect two bottles of methane gas by water displacement. To insure collecting pure methane, allow a *small* amount of the gas to escape before beginning the collection. Do not allow too much to escape or it will be difficult to fill the two collecting bottles. This observation is worthwhile since it illustrates the relatively poor yield or "inefficiency" which characterizes many organic reactions.

Test the methane which has been collected for combustibility by placing a collecting bottle upright on the table, removing the cover glass, and igniting the contents with a match or burning splint. Observe the characteristics of the flame as combustion occurs. Examine the mouth of the bottle for any residue of unburned carbon.

If a second bottle of methane has been collected, mix the gas with air by placing an identical gas collecting bottle over the bottle of methane, removing the cover plate, and placing the rims of the bottles in contact with each other. Within three to four minutes the methane and air should have thoroughly mixed. Test each bottle separately for the combustibility of the mixture inside.

Allow the test tube in which the methane was generated to cool. Test the residue for the presence of a carbonate by adding 10 ml. of dilute hydrochloric acid (see activity 4.66*a*). The carbon dioxide liberated will extinguish a burning splint which is lowered into the test tube.

If NaOH is considered as one of the active ingredients of the soda lime, the reaction for the preparation of methane is

$$NaC_2H_3O_2 + NaOH \rightarrow CH_4 + Na_2CO_3$$

Note: It is essential that this reaction be performed with anhydrous sodium acetate. If only the hydrated compound is available, it may be dehydrated by strongly heating an appropriate quantity in a porcelain crucible. Cool and pulverize the residue for use in the preparation.

The use of semimicro technique in organic chemistry is discussed in references *7R-3-4.*

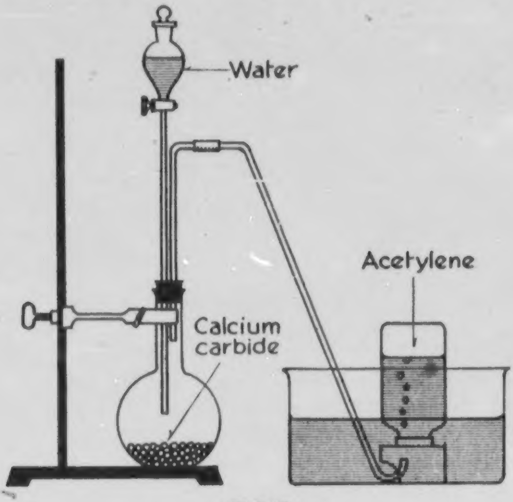
7.05. Preparation of Acetylene

TEACHER DEMONSTRATION ONLY: Arrange the apparatus as indicated in diagram 7.05. Place several lumps of calcium carbide in the 250-ml. flask and allow water to drip slowly on the calcium carbide so that acetylene gas is liberated at a steady rate. Allow a quantity of the gas initially evolved to escape, then collect two bottles of acetylene.

Place one of the bottles of acetylene upright on the demonstration table and ignite the gas with a match or burning splint. The sooty flame produced is quite dramatic, although a bit messy. The presence of carbon in the acetylene molecule is effectively demonstrated, as well as the need for a generous supply of air to improve combustion.

Place 5 ml. of dilute potassium permanganate solution, which has been acidified with 2 or 3 drops of dilute sulfuric acid, into the second bottle of acetylene and shake the bottle. This solution is commonly used as a test for saturation among hydrocarbons and is often referred to as *Baeyer's Solution.* If the color of the original solution is not too intense, it should be completely eliminated by reaction with the unsaturated acetylene molecule.

Test the gas in the laboratory with the potassium permanganate solution. There should be little color change since the hydrocarbon molecules of these gases are saturated.



7.05

7.06. Halogenation of Hydrocarbons

The various members of the halogen group form a great many organic compounds by becoming part of various hydrocarbon molecules. Such combinations are achieved most frequently either by substitution reactions in which one or more halogen atoms substitute for a like number of hydrogen atoms in a hydrocarbon molecule, or by addition reactions in which unsaturated hydrocarbons react with a halogen by the elimination of either a double or triple bond. Typically addition reactions occur more readily than substitution reactions and this can be shown by experimental observation.

a. Place 2 ml. of pentane (petroleum ether may be used if pentane is not available) in each of two test tubes to which 4 ml. of bromine water has also been added. Shake both test tubes; place one in a dark place and the other in sunlight or in front of a bright artificial light. Compare the contents over a period of 10 or 15 minutes. In the dark little or no reaction occurs. However, in the other tube light energy causes a reaction which eliminates the color of free bromine.

In the case of such substitution reactions half of the halogen atoms become part of the hydrocarbon molecule while the other half of the atoms combine with the hydrogen which has been removed.

$$C_5H_{12} + Br_2 \rightarrow C_5H_{11}Br + HBr$$

If sufficient bromine is available, the reaction can continue, producing molecules such as $C_5H_{10}Br_2$ and $C_5H_9Br_3$ and additional quantities of HBr.

b. Prepare a bottle of acetylene gas by the method described in activity 7.05 and add 4 ml. of bromine water to the bottle containing the acetylene. Shake the bottle and note the rapidity with which the bromine color disappears. This illustrates the ease with which the triple bond can be eliminated and the molecule saturated with bromine.

c. If either natural gas or "bottled" gas is used as a laboratory fuel fill a gas-collecting bottle with this gas by water displacement. Add 4 ml. of bromine water and compare the rate of reaction with that of the acetylene. This substitution reaction may also be speeded up by exposure to bright light.

7.07. Petroleum Distillation

a. TEACHER DEMONSTRATION ONLY: The principle of fractional distillation can be demonstrated by using the conventional distillation apparatus to obtain some of the better known fractions from crude petroleum. Set up the apparatus as shown in diagram 7.07*a*. While a 250-ml. distilling flask is desirable, it can be replaced, if necessary, by a Florence flask equipped with a two-holed stopper and delivery tube. Measure into the distilling flask 100 ml. of crude petroleum, using a funnel so that no petroleum runs into the side arms of the flask. Place a 25-ml. graduated cylinder under the outlet of the condenser. Place a 360°C. thermometer in the cork stopper so that the bulb extends just below the delivery arm of the flask.

Heat the petroleum gently and note the temperature at which the first drop gathers on the thermometer bulb. This is the initial boiling point of the petroleum sample. Raise the temperature slowly to 75°C. and collect the distillate until this temperature is reached. Note and record the volume. This is essentially light naphtha or petroleum ether and is used in considerable quantity as a commercial solvent. Place the distillate in a suitable container; label and stopper the container.

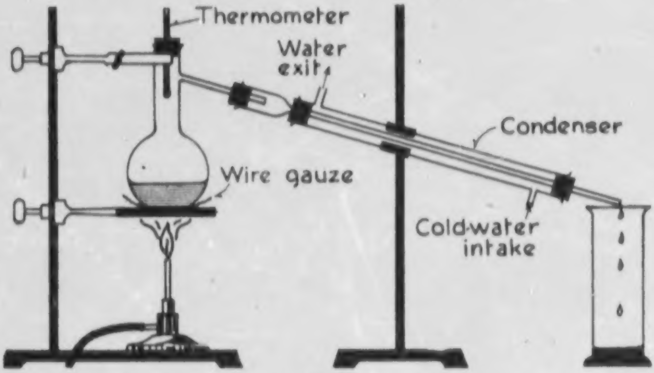
Raise the temperature of the distillation slowly to 200°C., again collecting the distillate in the graduated cylinder. Allow the temperature to drop to 175°C. and then bring it back up to 200°C. This fraction is raw gasoline and the volume approximates the "straight-run" yield. Record the volume; transfer to a labeled container and stopper.

At this point drain the water from the condenser and then collect the next fraction up to 275°C. Allow to cool and then reheat to 275°C. This is the kerosene fraction. Note the volume and transfer this fraction to a labeled container.

Raise the temperature to 300°C.; cool; then reheat to 300°C. This is the fuel oil fraction. Record the volume and transfer to a container.

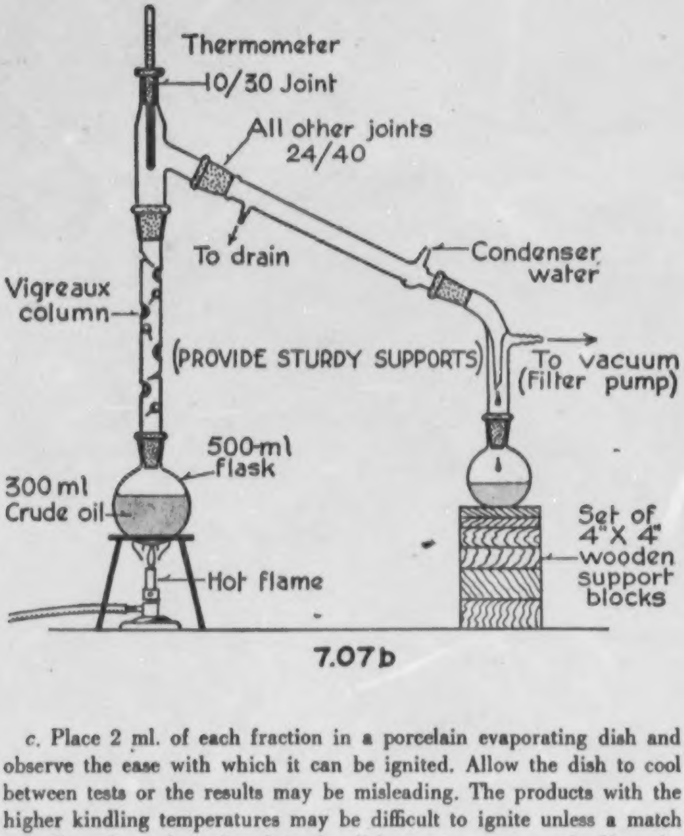
Obtain the final fraction by heating to about 340°C., allowing it to cool slightly, and then reheating to 340°C. This is the light lubricating oil fraction and should be so labeled. At this temperature range some cracking may occur which will deposit carbon (petroleum coke) in the flask.

After the residue has cooled, measure its volume. The residue contains various lubricants, vaseline, paraffin and asphalts. Use an organic solvent such as benzene to rinse the flask and condenser. *CAUTION: Vapor from benzene is toxic and should not be breathed.*



7.07 a

b. An alternate method for the fractional distillation of petroleum is shown in diagram 7.07*b*. This apparatus is usually not available in the ordinary high school chemistry laboratory because the more simplified apparatus serves just as well.


Thermometer
10/30 Joint
All other joints 24/40
To drain
Condenser water
Vigreaux column
(PROVIDE STURDY SUPPORTS)
To vacuum (Filter pump)
500-ml flask
300 ml Crude oil
Set of 4" X 4" wooden support blocks
Hot flame

7.07b

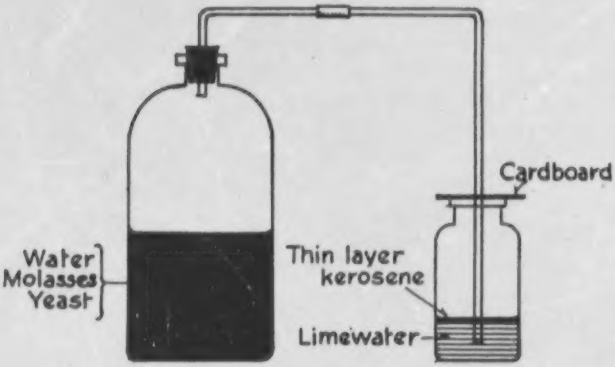
c. Place 2 ml. of each fraction in a porcelain evaporating dish and observe the ease with which it can be ignited. Allow the dish to cool between tests or the results may be misleading. The products with the higher kindling temperatures may be difficult to ignite unless a match or splint of wood is placed in the dish to serve as a wick. Note the type of flame and the residue left by each fraction.

7.08. Preparation of Ethyl Alcohol by Fermentation

The process of fermentation should be familiar to all chemistry students and can be best understood by actually preparing a fermentable mixture. Various carbohydrates may be used for this purpose, but either sucrose or molasses is usually most readily available.

Equip a 2-quart bottle (an empty acid bottle which has been thoroughly rinsed is satisfactory) with a one-holed rubber stopper and a delivery tube. Place a pint of molasses, a quart of water and half a yeast cake in the bottle. Mix thoroughly and set aside in a warm dark place. Run the end of the delivery tube into a widemouthed bottle half filled with limewater. Add a thin layer of kerosene to the bottle containing limewater in order to exclude air from contact with the limewater (see diagram 7.08). After the fermentation reaction has taken place for a short time, examine the limewater for evidence of the evolution of carbon dioxide gas. Allow the fermentation reaction to continue for five or six days. At the end of this period of time remove a small amount of the fermented mixture, filter it and test for the presence of ethyl alcohol.

To test for ethyl alcohol, dissolve a crystal of iodine in about 5 ml. of the filtrate in a test tube. Add 2M sodium hydroxide dropwise until a yellow coloration appears (iodoform). Heat the test tube to a temperature of approximately 60°C. and then allow to stand for a few minutes. The iodoform precipitates. The iodoform can be obtained as a dry powder by filtering the mixture and allowing the filter paper to dry.



7.08

7.09. Separation of Alcohol by Distillation

Place about 200 ml. of the fermented mixture prepared in activity 7.08 in a 500-ml. distilling flask, equip with a thermometer and a condenser, and distill. Collect 20 ml. of distillate; notice the temperature at which the distillate comes off. Place a few ml. of the distillate in an evaporating dish and attempt to ignite it. In this fraction the concentration of the alcohol should exceed 50 percent. Therefore, this fraction should burn. Determine the purity of the alcohol by finding its specific gravity by the bottle method (see activity 7.15*b*). Consult the *Handbook of Chemistry and Physics* for the percent concentration of the alcohol. Collect additional 20-ml. samples and similarly test. Note that the concentration of alcohol in the distillate diminishes as the distillation continues.

7.10. The Properties of Alcohols

The well-equipped laboratory should contain quantities of several of the alcohols so that various properties may be observed. A number of the monohydric alcohols, including methanol, ethanol, propanol, butanol and pentanol, should be available, as well as the dihydric alcohol, ethylene glycol, and the trihydric alcohol, glycerine.

Compare some alcohols with respect to such properties as boiling points, miscibility with water, combustibility and specific gravity.

a. Boiling Points. In determining the boiling points of the lower boiling point alcohols (below 100°C.), place a test tube partially filled with the alcohol in a beaker of water. Heat the water in the beaker until the alcohol boils. Suspend the thermometer over the liquid in the test tube so that the condensing vapors wet the sides of the test tube at least one inch higher than the level of the thermometer bulb.

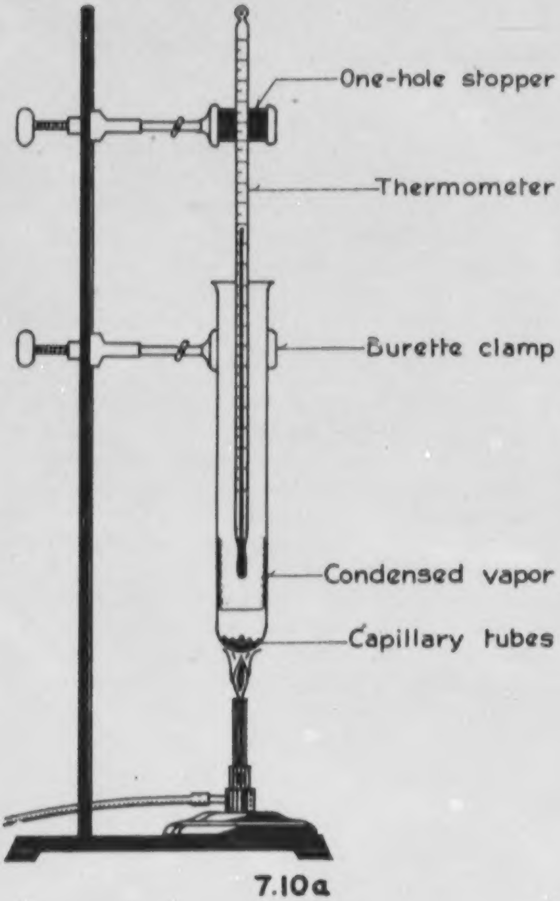
The boiling points of the higher boiling alcohols are probably best determined by a *TEACHER DEMONSTRATION ONLY* (see diagram 7.10*a*). The technique of using pieces of capillary tubes or boiling stones to prevent superheating and "bumping" is advised, both from the standpoint of safety and accuracy of boiling point determination. Prepare capillary tubes for this purpose by strongly heating a piece of soft glass tubing in a bunsen flame, drawing out the tubing and then breaking the thin tubing into half-inch lengths. Place three or four of these tubes in the liquid to be tested. Use new lengths for each separate boiling determination.

Consult a handbook for the boiling points of the corresponding hydrocarbons. Compare these boiling points with those of the alcohols. Relate to the polar nature of alcohols.

b. Miscibility. In observing the miscibility of alcohols with water, try a variety of proportions in order to make the observations somewhat quantitative. Ratios of 1:20, 1:5, 1:1, 5:1 and 20:1 (alcohol: water) will give evidence for some fairly definite conclusions. Pupils should become aware of the fact that the tendency to dissolve in water is much more common among the alcohols than among other groups of organic compounds.

c. Combustibility. Determine the combustibility of the alcohols by placing 2 or 3 ml. of the alcohol in an evaporating dish and igniting it. Note carefully the nonluminous flame produced by the less dense alcohols. With the high boiling point alcohols, such as ethylene glycol and glycerine, it will probably be necessary to use a match stick or a piece of paper as a wick in order to vaporize and ignite the alcohol. Note the correlation between the ease of ignition and the boiling point of the alcohol. The alcohols, like the hydrocarbons, burn only in the vaporized state.

d. Specific Gravity. The specific gravity of the alcohols may be determined either by the bottle method (see activity 7.15*b*) or by the use of appropriate hydrometers. Demonstrate the use of an hydrometer


One-hole stopper
Thermometer
Burette clamp
Condensed vapor
Capillary tubes

7.10a

to determine the concentration of a methanol-water or ethanol-water mixture. Consult reference tables in the *Handbook of Chemistry and Physics* to relate specific gravity to percent concentration. Refer to the use of the hydrometer in testing automobile antifreeze.

7.11. The Preparation of "Solid" Alcohol

Place 10 ml. of a saturated solution of calcium acetate in a 250-ml. beaker and add 60 ml. of either methyl alcohol or ethyl alcohol (denatured). A semisolid gel should quickly form. Place a small quantity of this gel on an asbestos pad and ignite it. The pale blue flame produced is characteristic of the alcohol being burned. This illustrates the preparation of "canned heat."

7.12. Phenol

CAUTION: Great care should be observed in handling phenol since it is a highly corrosive and poisonous substance. Do not allow it to come in contact with the skin; it can cause serious burns.

a. Demonstrate the limited solubility of phenol in water.

Explain that a 2.5 percent solution has excellent antiseptic properties and has been known by the common name of carbolic acid.

Test the water solution of phenol with a *pH* indicator. Show that the *pH* is below 7, and therefore somewhat acidic; hence the name, carbolic acid.

b. A fairly sensitive color test for phenol can be observed by adding a few drops of ferric chloride solution to about 5 ml. of phenol solution in a test tube. For purposes of comparison add a similar amount of ferric chloride solution to 5 ml. of a dilute solution of an aliphatic alcohol, such as methanol. In the case of the phenol-ferric chloride mixture the resulting coloration may be so intense that dilution may be required to identify the color.

c. The compound tribromophenol may be readily prepared from the water solution of phenol by placing 5 ml. of this solution in a test tube and adding bromine water until the color of the bromine is no longer removed. Separate the precipitate of tribromophenol by filtration. The reaction may be represented as:

$$C_6H_5OH + 3Br_2 \rightarrow C_6H_2OHBr_3 + 3HBr$$

Note that this substitution reaction occurs readily and requires very little time and energy. For purposes of contrast add 2 ml. of bromine water to 5 ml. of benzene in a test tube. Shake the tube and observe over a period of time to determine whether a similar substitution reaction occurs with benzene. The reaction in this case is very slow, but it can be speeded up by exposing the mixture to sunlight or a bright incandescent lamp. The conclusion may be drawn that apparently the presence of the OH group on the benzene ring (phenol) greatly facilitates the halogen substitution reaction.

7.13. Preparation of Formaldehyde

The oxidation of primary alcohols and the formation of various aldehyde compounds is a fundamental and significant type of organic reaction.

A dilute solution of formaldehyde can be prepared by the reaction between hot cupric oxide and methyl alcohol. Place 2 ml. of methyl alcohol and 5 ml. of water in a test tube which is partially immersed in a beaker of cold water. Make a spiral of copper wire by winding it 10 or 15 times around a pencil and then withdrawing the pencil. Have the spiral about 1 inch in length with about 8 inches of wire to serve as a handle. Heat the spiral in the bunsen flame to red heat and then plunge it into the methyl alcohol solution in the test tube. Repeat this procedure five or six times, or until a pungent odor, quite unlike the odor of methyl alcohol, becomes apparent. The copper is first oxidized by air:

$$2Cu + O_2 \rightarrow 2CuO$$

The alcohol is then oxidized to formaldehyde:

$$CH_3OH + CuO \rightarrow HCHO + Cu + H_2O$$

Note that the wire, which had darkened when held in the bunsen flame, becomes bright when dipped into the alcohol solution.

7.14. Reducing Property of Formaldehyde

a. Place 1 ml. of each of Fehling's solution *A* and *B* (or Benedict's solution) in a test tube and add a few drops of 40 percent formaldehyde solution (Formalin). Boil the mixture gently for a minute or two and observe the color change. The formation of the brick red cuprous oxide, or possibly some metallic copper, results from the reduction of the Cu^{++} ions in the test reagent. This reaction is typical of the aldehyde group as a reducing agent. It is essentially identical to the reaction which occurs when certain sugars produce a reducing action on either Fehling's or Benedict's solution.

b. Place 3 ml. of silver nitrate solution in a very clean test tube and add slowly dilute ammonium hydroxide (1 part of stock solution to 9 parts of water) until the precipitate which first forms has almost dissolved. Add 2 drops of 40 percent formaldehyde solution, shake the tube and warm it gently. Note the deposition of silver on the sides of the test tube as a mirror. (The silver may later be dissolved and removed with nitric acid.)

The formation of metallic silver is also a reduction reaction brought about by the aldehyde:

$$2AgOH + HCHO \rightarrow 2Ag + H_2O + HCOOH \quad \text{(formic acid)}$$

7.15. Preparation of Acetic Acid and Determination of Purity

a. While the method is not used commercially, it will be of interest to prepare a sample of acetic acid by the reaction of sulfuric acid on sodium acetate. This reaction is typical of the salts of organic acids and is used in the preparation of some of the long-chain fatty acids from soaps.

Place 40 gm. of anhydrous sodium acetate in a 250-ml. distilling flask. To this add cautiously 25 ml. of concentrated sulfuric acid. Use a funnel with a long enough stem to bypass the delivery arm of the flask when adding the acid. The acid may run out of the delivery arm if it is poured in without this precaution. If the mixture becomes so hot that loss of vapor is threatened, cool the flask in tapwater.

Attach a condenser to the flask, place a thermometer in a one-hole cork stopper at the top of the flask, and attach the necessary hoses for water circulation (see diagram 7.07*a*). Heat the mixture carefully, keeping the temperature in the flask below 125°C. during the distillation. Collect about 20 ml. of distillate in a graduated cylinder.

The acetic acid so prepared is of high concentration, as will be noted from the strong odor.

A dilution of about 20 parts of water to 1 part of the distillate would approximate a typical vinegar concentration. Dilute a portion of the distillate. Test for weak acid behavior, such as by observing its action on pieces of zinc and magnesium ribbon, effect on litmus and reaction with a carbonate or bicarbonate.

b. The percentage of acetic acid in the distillate can be determined by calculating the specific gravity of the distillate. The specific gravity of aqueous acetic acid solutions and percent composition may be found in the *Handbook of Chemistry and Physics.* To determine the concentration of an acid by titration, see activity 5.21.

To determine the specific gravity of the distillate, weigh an empty 10-ml. specific gravity bottle and stopper (pycnometer) carefully (see page 263, diagram 7.15*b*). Then fill the bottle with the distillate. Insert the stopper (the excess solution will spill out through the hole in the stopper), dry the outside of the bottle, and again weigh carefully. In this situation it may be assumed that an equal volume of distilled water will weigh 10.00 gm. The specific gravity of the distillate can be found from the equation:

$$\text{Specific gravity} = \frac{\text{weight of liquid}}{\text{weight of equal volume of water}}$$

To illustrate: A 10-ml. specific gravity bottle weighs 12.30 gm. empty and 22.87 gm. when filled with distillate. 22.87 gm. — 12.30 gm. = weight of distillate (gm.)

$$\text{Sp. gr.} = \frac{10.57\text{ gm.}}{10.00\text{ gm.}} = 1.057$$

A check in the *Handbook of Chemistry and Physics* indicates that an aqueous acetic acid solution with a specific gravity of 1.057 contains 97 percent acetic acid.

7.16. General and Specific Properties of Organic Acids

Obtain quantities of a variety of organic acids, including, if possible, the following: acetic, butyric, lactic, oxalic, succinic, citric and stearic acids. Use these acids to demonstrate some properties of organic acids.

a. **Ionization of Acids.** The organic acids are unique among the common types of organic compounds in that they ionize, but only to a slight degree. They do, however, display many of the typical acid properties.

(1) Place 5 ml. of 1 Molar solutions of such acids as acetic, oxalic, citric and succinic acid in separate test tubes. Place a drop of each acid on blue litmus paper as a test for hydrogen ions.

(2) Drop a small piece of magnesium ribbon into each test tube. Observe the evidence of reaction and whether there is a significant difference in the rates of reaction.

(3) Rinse the test tubes and place 0.5-gm. portions of sodium carbonate in each test tube. Add 5 ml. of each of the acids to separate test tubes. Observe the characteristic acid reaction and the similarity to the behavior of inorganic acids.

b. **Physical State of Acids.** Note that only the first three of the named organic acids (those with relatively low molecular weights) occur as liquids at room temperature. This is in contrast with inorganic acids, where the liquid state is typical of this group of compounds.

c. **Odor of Acids.** Observe the odor of dilute acetic acid, butyric acid and lactic acid. Associate these odors with the familiar substances in which these compounds occur. Generally, as the molecular weight increases, the saturated aliphatic mono-carboxy acid tends to change from an odorous to an odorless compound.

d. **Solubility of Acids in Water.** Observe the physical appearance of stearic acid. Rub a little between the fingers and note the feel.

Place a very small quantity in two separate test tubes and test for solubility by adding 3 ml. of ethyl alcohol to one test tube and the same quantity of water to the other. The stearic acid is more soluble in ethyl alcohol than in water. Compare the solubilities of acetic acid and stearic acid in water. Generally, for saturated aliphatic monocarboxy acids, as the molecular weight increases, the solubility in water decreases.

e. **Oxalic Acid as a Reducing Agent.** Place 5 ml. of the 1M oxalic acid solution in a test tube. Add dropwise a dilute potassium permanganate solution until the oxalic acid no longer eliminates the color of the potassium permanganate solution. This change demonstrates the color removal or "bleaching" capacity of oxalic acid which is sometimes utilized in bleaching wood surfaces and in removing iron rust stains from various surfaces.

$$2KMnO_4 + 8(COOH)_2 \rightarrow 10CO_2 + 2MnC_2O_4 + K_2C_2O_4 + 8H_2O$$

Try adding the potassium permanganate solution to the 1M acetic acid solution to determine whether a similar "bleaching" effect is produced.

f. **Test for Acetate Ions.** Place 5 ml. of 1M acetic acid in a test tube, drop in a small piece of litmus paper, and add dilute sodium hydroxide solution with stirring until the litmus just turns blue. Now add 2 ml. of ferric chloride solution, note the appearance of the mixture, and heat it until a change occurs. The resulting brown color is due to the formation of basic ferric acetate which has the formula $Fe(OH)(C_2H_3O_2)_2$.

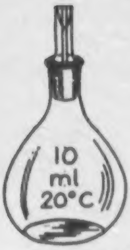
Repeat the test with one of the other acids, such as citric acid, to show that the color obtained is a specific test for the acetate ion.

g. **Citric Acid as a Flavoring Agent.** Place about 50 ml. of cold water in a 250-ml. beaker and add, with stirring to dissolve the substances, small quantities of citric acid (powder) and sucrose (table sugar). If only small quantities at a time are added, and the concentration is carefully adjusted, it should be possible to produce a reasonably palatable imitation of lemonade.

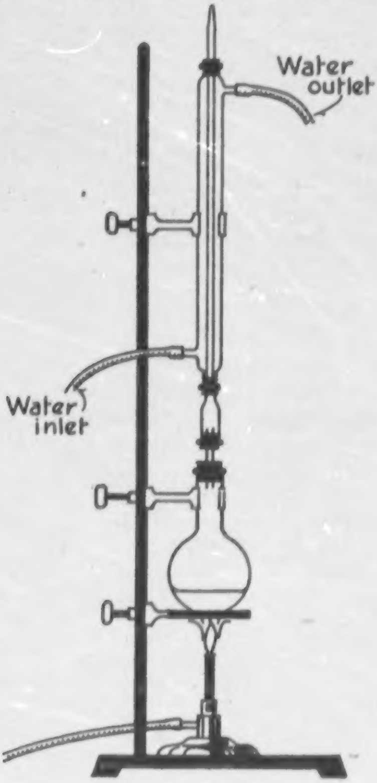
7.17. Esterification

Esters are most frequently prepared by the reaction of alcohols and acids in the presence of concentrated sulfuric acid. When the acid used is an organic acid, many of the esters resulting from such reactions have odors characteristic of certain fragrances produced by plants. It is possible to prepare various esters in the laboratory which pupils may readily recognize. It is also worthwhile to have on hand in the chemical stockroom small quantities which can be identified by odor.

a. **Preparation of Ethyl Acetate.** Place 25 ml. of ethyl alcohol (denatured alcohol is satisfactory) in a 250-ml. flask. Add 5 ml. of concentrated sulfuric acid and 25 ml. of glacial acetic acid. Boil this mixture gently with a condenser in the reflux position (see diagram 7.17*a*) for 20 to 30 minutes. Contrast this rate of reaction with a typical neutralization reaction as encountered in inorganic chemistry.



7.15b



7.17a

Transfer the mixture carefully to a distilling flask, equip the flask with a condenser, and distill until approximately 30 ml. of distillate have been collected. The temperature should go no higher than 100°C.

Since the distillate is impure and contains particularly a quantity of unreacted acetic acid as well as some alcohol, steps must be taken to obtain a reasonably pure sample of ethyl acetate. Pour the distillate into a beaker and neutralize the excess acetic acid with a saturated solution of sodium carbonate until a piece of red litmus placed in the mixture turns blue. Pour this mixture into a separatory funnel and extract the upper layer, which is essentially ethyl acetate.

Many pupils will recognize the odor of the ethyl acetate and the girls will usually associate this with "fingernail polish remover." Some may even volunteer to try it out for this purpose. Demonstrate the solvent property of the ethyl acetate by soaking a quantity onto a cloth or paper towel and rubbing along a lacquered surface such as a pencil.

b. Odors of Esters. The odors of other esters can be observed by gently heating mixtures of small amounts of the following chemicals in a test tube. A few drops of concentrated sulfuric acid should be added in each case. The heating is best accomplished by placing the test tube in a beaker of heated water and allowing adequate time for the esterification reaction to occur.

(1) 5 ml. of methyl alcohol and 2 gm. of salicylic acid

(2) 5 ml. of ethyl alcohol and 5 ml. of butyric acid

(3) 5 ml. of n-amyl alcohol and 5 ml. of acetic acid

The table below gives a few examples of some of the natural essences which can be duplicated by organic esters. In virtually all cases of natural essences the odor is due to a mixture of several, perhaps dozens, of esters and aldehydes. The table indicates only the one or two main ingredients.

ESSENCE	ESTER	ESSENCE	ESTER
Apricot	Amyl butyrate	Pineapple	Ethyl butyrate
Banana	Amyl acetate	Raspberry	Isobutyl formate Isobutyl acetate
Grape	Ethyl formate Ethyl heptoate	Rum	Ethyl butyrate
Orange	Octyl acetate	Wintergreen	Methyl salicylate

7.18. Polymerization

One of the really significant objectives of any study of organic chemistry, regardless of how brief such an experience may be, should be to gain an understanding and appreciation of the polymerization process. Since so many organic compounds, both natural and synthetic, are actually polymers formed in most cases from comparatively simple small molecules, the desirability of a pupil acquiring an insight into the mechanisms of such reactions is obvious. These polymers are the basis of various industrial products, including plastics, synthetic textiles, rubber and fuels. It is possible to demonstrate the preparation of several such products and thereby stimulate the imagination of the pupils as to the limitless possibilities of polymerization reactions.

a. **Bakelite.** This is one of the first successful synthetic plastics, having been originally developed by Baekeland and produced commercially in 1907. It is still a very popular plastic and has the largest annual production of any of the so-called phenolic resins. This plastic is produced by the reaction of phenol and formaldehyde, under proper conditions of temperature control and aided by an appropriate catalyst. The product formed is of a thermosetting type and is a cross-linked polymer.

Place 25 gm. of phenol and 50 ml. of 40 percent Formalin (formaldehyde) solution in a 250-ml. Erlenmeyer flask. Add 3 ml. of 40 percent sodium hydroxide, which will act as a catalyst. Heat this mixture under a hood at 107°C., or in a flask equipped with a condenser in the reflux position (see diagram 7.17*a*). If the latter setup is used, boil the mixture gently. In either case continue heating until the mixture has become quite viscous, with a consistency similar to that of honey or molasses. This will probably require approximately 45 to 60 minutes of heating.

Pour this viscous product into a suitable mold for subsequent "curing." If the solution is allowed to cool at this point it will be a resinous substance that will melt again on slight heating and dissolve in many organic solvents. To complete the process of polymerization bake the resin for several hours at moderate temperature. If a drying oven is available, "bake" the resin for 2 hours at 50°C. and then at 75°C. for 2 hours. By the end of this time the product should have become a hard, glossy, ruby-red solid which now has a very high melting point and can be shown to be impervious to the effects of most organic solvents. If no drying oven is available, "curing" can be accomplished by placing the mold on an asbestos mat and placing it over a 100-watt bulb in a photographic reflector. Adjust the distance between the mold and bulb to approximate the recommended temperature.

b. **Nylon.** One of the easiest polymerization reactions to produce and one of the most fascinating to observe is the reaction which produces a long-chain linear polymer of the nylon type. This reaction is unique among organic reactions of this sort in that it occurs fairly rapidly and requires no external application of energy.

Prepare a solution of 2 ml. of sebacyl chloride (or other chloride of a dicarboxylic acid) in 100 ml. of carbon tetrachloride in a 200-ml. tall-form beaker. Over this carefully pour a solution of 4.4 gm. of hexamethylenediamine in 50 ml. of water. A polymeric film forms at once at the interface of the two solutions. Grasp this film at the center with tweezers and raise as a rope of continuously forming polymer film. The effect is especially striking if a revolving drum is first made, using an oatmeal box or similar container, running a dowel through the middle to serve as an axle and attaching a short handle so that the drum can be turned. Attach the end of the polymer film to the drum and wind continuously around it until one of the solutions has been used up.

c. **Thiokol (Synthetic Rubber).** Synthetic rubber is an example of one of the polymers of great importance in present-day industrial production. The preparation of one of the types of synthetic rubber as a laboratory experience not only lends interest but also illustrates some of the chemistry of polymers.

Thiokol and similar sulfur polymers may be prepared by the polymerization of an alkali or alkaline earth metal polysulfide and a halogen substituted olefinic hydrocarbon. The amount of sulfur in the polysulfide determines the elastic quality of the rubber.

In a 250-ml. beaker containing 100 ml. of water dissolve 4 gm. of sodium hydroxide and heat to boiling. Add 10 gm. of flowers of sulfur. Stir until all the sulfur has dissolved. The liquid will turn from a light yellow to dark brown color as the sulfur content of the polysulfide increases. If the sulfur does not dissolve completely in 10 to 15 minutes, allow the solution to cool and decant the dark brown liquid from the undissolved sulfur. To this liquid add 20 ml. of ethylene dichloride while maintaining the mixture at a temperature of 80°C. Stir the mixture constantly until a spongy lump of synthetic rubber forms at the bottom of the beaker.

Remove the synthetic rubber from the beaker and wash thoroughly. Its color will vary from white to yellow and it will have a degree of elasticity depending on the sulfur content of the polysulfide. This polymer will resist organic solvent action, a characteristic which distinguishes it from natural rubber. In actual use it is mixed with carbon, zinc oxide and some natural rubber to make it harder and to give it better wearing qualities.

7.19. An Introduction to Biochemistry

A study of organic chemistry is scarcely complete without at least a brief look at the three major classes of compounds which are the chief components of our foods, namely the carbohydrates, fats and proteins. These can be studied as examples of types of compounds already encountered, not as unique types of compounds themselves. Note the close relationship of carbohydrates to aldehydes and ketones, fats to esters and proteins to polymers of amino acids and various nonprotein groups. Various properties and typical reactions of these compounds can be readily observed. See reference *7R-5*.

a. Carbohydrates.

(1) **Composition.** Place 5 gm. of sucrose in a 100-ml. beaker. Add 5 ml. of concentrated sulfuric acid and observe the mixture for several minutes for evidence of chemical change. Note the loss of water vapor from the beaker and the residue of carbon which remains. Infer the composition, of sucrose, and other carbohydrates, from this reaction.

(2) **Physical Properties.** Exhibit samples of a variety of carbohydrates, including, if possible, glucose, fructose, sucrose, lactose, maltose, starch and dextrin. Taste the various carbohydrates and attempt to arrange them in order of sweetness. Introduce a sample of saccharine to show that sweet taste is not necessarily a property of sugar only. It will also become apparent that the sugars themselves vary considerably in this property, from fructose as one extreme to lactose as the least sweet of the aforementioned sugars.

Test the various carbohydrates for solubility by weighing out 0.5 gm. of each and attempting to dissolve it in a test tube containing 20 ml. of water. Starch and dextrin do not dissolve readily as do all the sugars. Relate to the lack of taste sensation produced by these less soluble carbohydrates.

(3) **Reducing Action of Carbohydrates.** Place 5 ml. of each of the carbohydrate solutions resulting from the solubility tests in (*2*) above in separate test tubes. Add 2 ml. of Benedict's (or Fehling's) solution to each test tube. Place all the test tubes in a beaker of hot water at 80°C. to 90°C. Note the evidence of reduction of cupric ions to red cuprous oxide in some of the solutions. Not all carbohydrates act as reducing agents. Sucrose is a nonreducing sugar.

(4) **Hydrolysis of Sucrose.** Place 5 ml. of sucrose solution in a test tube and add 3 drops of hydrochloric acid. Boil this mixture gently for five minutes and then neutralize the acid by adding solid sodium carbonate until the mixture no longer effervesces. Add 2 ml. of Benedict's solution and warm the mixture as previously tested. The solution should now show a reducing action on the Benedict's solution as evidenced by the appearance of a brick red color.

The sucrose has been hydrolyzed to a mixture of glucose and fructose, both of which are reducing sugars. This same hydrolysis reaction would occur much more slowly if the sucrose solution were boiled for a sufficient length of time. This is one of the reactions that takes place when sucrose is used in preparing jams and jellies. Demonstrate a similar hydrolysis reaction by using starch instead of sucrose, treating it in the same way with hydrochloric acid and boiling.

b. Cellulose. This complex polysaccharide forms a large portion of the cell walls and supporting structure of plants. It is insoluble in most of the common solvents, has a more complex structure than the starches and is not so readily hydrolyzed. Its resistance to hydrolysis makes it virtually indigestible by nearly all organisms. Therefore, it has very little value as a food material, but is significant for the wide variety of uses that are made of it. Absorbent cotton and filter paper are almost pure cellulose and may be used in the following experiences as typical examples of cellulose.

(1) **Parchment Paper.** Dip a strip of filter paper into a cold solution of sulfuric acid (2 vols. of concentrated sulfuric acid to 1 vol. of water). After 15 seconds transfer the paper to a beaker filled with cold water. Wash thoroughly with water, then with very dilute ammonium hydroxide. Rinse out all the ammonium hydroxide with water and allow to dry. Compare the treated paper with the original filter paper to show an interesting difference in texture and strength.

(2) **Preparation of Cellulose Acetate (Acetylation).** Dissolve 0.5 gm. of filter paper (torn into small pieces) in a mixture of 20 ml. of glacial acetic acid and 6 ml. of acetic anhydride, with 2 drops of concentrated sulfuric acid added as a catalyst. Inasmuch as it will probably require about 24 hours for the reaction to occur, the mixture should be covered and allowed to react for such an interval. Occasional stirring or agitation will help to bring about a more complete reaction.

After the filter paper has completely dissolved, pour the resulting mixture in a thin stream into cold water in a large beaker (600 ml.). Filter to obtain the precipitated cellulose acetate, press out the excess water, and spread it out to dry on a filter paper. *CAUTION: Use the hood.* Dissolve the thoroughly dry cellulose acetate in 20 ml. of acetone in a large test tube. Pour some of this solution onto a glass surface, such as a watchglass, and allow the acetone solvent to evaporate. A thin film of cellulose acetate should remain on the glass. This can usually be loosened by running some water over it. Remove the film, observe its appearance, and cautiously test for flammability.

(3) **Preparation of Rayon (Cuprammonium Process).** Dissolve 5 gm. of cupric sulfate in 100 ml. of boiling water, and add sodium hydroxide until precipitation is complete. Filter and wash the precipitate well, and dissolve it in a minimum quantity of ammonium hydroxide. *Note:* An alternate method of preparation is to bubble a slow stream

of air through 100 ml. of strong ammonium hydroxide containing 15 gm. of fine copper turnings. Continue this procedure for one hour.

Add a sheet of shredded filter paper to 25 ml. of this solution (Schweitzer's reagent) in a small beaker. Stir until the paper has dissolved. Pour the solution in a fine stream or squirt it from a medicine dropper or pipette into 250 ml. of 1 Molar sulfuric acid solution. The substance formed is regenerated cellulose or rayon. In industry the cellulose solution is squirted through the tiny holes of a spinneret into the acid to produce threads of rayon. Cellophane is regenerated cellulose manufactured in sheet form.

c. **Fats.** Inasmuch as the pupils have become acquainted with the process of esterification earlier in the discussion of organic chemistry, it should not be difficult for them to understand the basic structure of the fat molecule as an ester of the tri-hydroxy alcohol, glycerin, combined with various acid molecules. Illustrate the combination of glycerin with such common fatty acids as stearic acid ($C_{17}H_{35}COOH$) and oleic acid ($C_{17}H_{33}COOH$). Oleic acid has one double bond in the carbon chain. The "so-called" unsaturated fats are esters of unsaturated acids.

(1) **Solubility.** Place a few drops of a fat or oil in several clean, dry test tubes. Add 5 ml. of water to one tube and similar volumes of various organic solvents, such as ethyl alcohol, ether, chloroform, carbon tetrachloride and acetone, into the others. Shake each tube and observe which solvents dissolve fat.

Place a few ml. of one of the solutions of fat on a filter paper and allow the solvent to evaporate. The translucent spot which remains is sometimes used as an indication of the presence of fats in foods, when one of these solvents is used as a means of extraction.

(2) **Emulsification.** Shake a mixture of 3 drops of cottonseed oil and 5 ml. of water in a test tube. After thorough mixing, note the time required for the separation of the two liquids. Add a few drops of soap solution to the mixture, shake, and again observe for separation. Repeat the procedure by using a few drops of liquid detergent instead of soap. When soap or detergent is added, the fat becomes emulsified and the small particles remain suspended for a considerable length of time. Discuss the relationship of this behavior to the cleansing effect of soaps and detergents.

(3) **Saturated and Unsaturated Fats.** Place 5 or 6 drops of melted butter and raw linseed oil in separate test tubes. Add 4 ml. of a dilute solution of iodine in carbon tetrachloride to each test tube. Observe any tendency of the iodine color to disappear. The reaction of unsaturated fats with "free" iodine varies with the degree of unsatura-

tion. Test other fats in a similar manner and compare the results.

Discuss the concept of the "iodine number," which is the number of grams of iodine which react with 100 gm. of a given fat. The contrast between linseed oil, a highly unsaturated fat having an iodine number between 175 and 202, and butterfat, a relatively saturated fat with iodine numbers of 26 to 28, is quite obvious. Other common fats have iodine numbers as follows:

Coconut oil	6.2— 10	Olive oil	79— 88
Corn oil	111—128	Peanut oil	88— 98
Cottonseed oil	103—111	Tung oil	163—171

Note from the above values that it is the highly unsaturated oils (with high iodine numbers) such as linseed oil and tung oil, which can be oxidized by the atmosphere. Therefore, they serve as drying oils in paints and varnishes.

(4) **Saponification.** Dissolve 2.5 gm. of solid sodium hydroxide in 15 ml. of 50 percent isopropyl alcohol (prepared with distilled water) in a 150-ml. beaker. Add 6 ml. of cottonseed oil and heat the mixture, with constant stirring, for about 30 minutes. Use a small flame and avoid vigorous boiling. Add 50 percent alcohol as needed to maintain a constant volume of liquid in the beaker.

After heating for the indicated time interval, pour the mixture into a 250-ml. beaker containing 150 ml. of saturated sodium chloride solution. Filter the mixture to obtain the soap which separates in this "salting out" process. Wash the soap with 10 ml. of ice-cold distilled water. Test the soap which remains on the filter paper for sudsing action by mixing a small amount of the soap with 5 ml. of distilled water in a test tube and shaking the mixture thoroughly. The appearance of suds indicates a successful saponification reaction.

d. **Proteins.**

(1) **Composition.** The presence of nitrogen in proteins can be detected by the reaction with soda-lime, which causes the formation and release of ammonia gas. The typical analysis of protein for nitrogen content is based on the quantitative determination of the ammonia which is released when the protein is decomposed.

Mix 0.5 gm. of either casein or powdered egg albumin with an equal weight of soda-lime in a test tube. Shake the tube to mix the solids and warm in a bunsen flame. Cautiously note the odor of the gas evolved and test it with moist litmus paper.

To show the presence of the elements, carbon and sulfur, in proteins, place enough powdered egg albumin in a test tube to cover the bottom of the tube and heat the tube. Hold a piece of moist lead acetate paper at the mouth of the test tube. The color change indicates the presence of sulfur. The material in the bottom of the test tube will char. This suggests the presence of carbon.

(2) **Identification.** Proteins, as well as certain other substances, give a violet color in the presence of the cupric ion and dilute alkali. This is known as the *biuret reaction*. Place 5 ml. of either casein or egg albumin solution in a test tube and add 2 ml. of 3N sodium hydroxide. Shake the mixture for a few seconds and add a drop of 0.2N cupric sulfate solution. As a control, perform the same test on a similar quantity of sucrose solution.

Since most proteins contain amino acids which have an aromatic ring, they are readily nitrated on treatment with concentrated nitric acid. The products are yellow, and the color is deepened by treatment with a base. This test is known as the *xanthoproteic test*. Place 3 ml. of egg albumin or casein solution in a test tube, add 1 ml. of concentrated nitric acid and heat to boiling. After noting the color, cool the test tube under the water tap and cautiously add 3N sodium hydroxide solution until the mixture is basic. Many pupils have inadvertently performed a similar test on either their skin or fingernails when nitric acid is accidentally spilled on the fingers.

(3) **Coagulation.** Many proteins which are soluble in water can be rendered insoluble by the action of heat or various chemicals. The formation of the coagulated form occurs, in many cases, during the digestive process and may be an essential part of that process. The action of several coagulating agents may be readily demonstrated.

Place 5 ml. of egg albumin solution in a test tube and heat to boiling. The change of the soluble albumin to a coagulated form is typical of the behavior of many soluble proteins.

To show the coagulating effect of the enzyme rennin, add a pulverized junket tablet to half a test tube of milk. Warm the mixture. In this case the milk protein, casein, is quickly coagulated by the enzyme rennin, of which the junket tablet is composed.

7.20. Dyes and Dyeing

The coloring or dyeing of fibers is an ancient art. In the early days natural pigments or dyes were used; now most dyes are synthetic organic compounds. The problem of satisfactory dyeing is not, however, limited to the production of a compound of appropriate color, but is complicated by necessity of causing the dye to adhere to the fabric. The molecules of some dyes have groups by which they become attached to certain fabrics. Other dyes require an adsorbing material (mordant) to attach the dye molecules to the fiber. A direct dye is one which is satisfactory when used alone. Since the nature of the fabric is also very important, dyes which are direct dyes for certain fabrics, such as silk or wool, may not be direct dyes for other fabrics, such as cotton.

a. **Preparation of a Dye-Like Material, Phenolphthalein.** There are many dyes whose color in solution depends on the acidity or alkalinity of the solution. Such a dye is called an indicator; phenophthalein is a very important example.

Place 0.1 gm. of phenol and an equal weight of phthalic anhydride in a test tube, add 1 drop of concentrated sulfuric acid and heat gently in and out of a small bunsen flame until the anhydride is just melted. Continue heating gently for about three minutes. Allow the test tube to cool and add 5 ml. of distilled water and just enough 1N sodium hydroxide solution to effect a color change. Filter the resulting solution and add sufficient 1N hydrochloric acid to remove the color. Observe that the color may be restored by adding an excess of sodium hydroxide.

b. **Direct Dyeing.** Prepare a dye bath by adding 10 ml. of 0.5 percent methyl violet solution to 90 ml. of water in a 250-ml. beaker. Heat the solution to boiling and place a piece of wool in the hot bath. Remove the flame and allow the wool to remain in the bath for two minutes. Remove the cloth and wash it with water.

Repeat the above procedure, using cotton cloth instead of wool and using the same dye bath. It will be observed that, while the wool fibers retain a substantial amount of the dye, very little dye is retained by the cotton fibers. Retain the dye bath for activity 7.20c.

It can be shown, however, that cotton fibers do have the capacity to retain certain dye materials (substantive dyes) and that Congo red is an example of such a dye. Prepare a Congo red solution by dissolving 0.5 gm. of sodium carbonate, 0.5 gm. of sodium sulfate and 0.1 gm. of Congo red in 50 ml. of water. Heat this solution to boiling and immerse a strip of wet cotton in it. Continue the boiling for five minutes. Remove the cloth, rinse it, and note that the dye is firmly attached to the cloth.

c. **Mordant Dyeing.** Most dyes will dye animal fibers (wool, silk) directly, but will dye vegetable fibers (cotton, linen) only when mordants are used. In this case the mordant attaches itself to the fiber and the dye attaches itself to the mordant.

Prepare a mordant solution by dissolving 0.5 gm. of tannic acid in 100 ml. of water. Heat the tannic acid solution to boiling and place a piece of cotton cloth, such as cheesecloth, in the hot solution. Reheat the methyl violet dye bath used in the direct dyeing process. Transfer the cotton cloth to the dye bath after first squeezing out the excess tannic acid solution. After two minutes remove the cloth from the dye and wash it with water. A comparison of the results of the procedures in which the cotton was placed directly in the methyl violet dye bath and then later was first treated with a mordant shows the effect of the mordant.

d. **Vat Dyeing.** Certain dyes, because of solubility characteristics, are most readily applied to cloth in a reduced and colorless form. The dyes develop color when they are oxidized by exposure to aid. Indigo is such a dye, and its behavior is typical of dyes in this group.

Prepare a colorless solution of indigo by placing 10 ml. of distilled water in a 6-inch by 1-inch test tube. Heat the water to boiling and then add a pea-sized pinch of indigo blue powder. Stir this mixture and add 0.5 gm. of ferrous sulfate. Again stir the mixture and add 30 ml. of concentrated ammonium hydroxide. Place the tube in a 250-ml. beaker containing 200 ml. of water which has been heated to boiling. Allow the test tube to stand in the beaker of hot water until the solid material has settled, leaving a considerable portion of clear liquid. Wet a piece of cotton cloth and dip it into the clear liquid in the test tube. Remove the cloth, note the color, and observe the change which occurs as the cloth is exposed to air for several minutes. Note also that the colored indigo is insoluble in water and is retained by the cloth when the cloth is rinsed or washed.

7.21. Fuel Cells

The fuel cell can convert chemical energy released by the oxidation of a fuel directly to electrical energy. It is this ability of converting chemical energy directly to electrical energy continuously and with twice the efficiency of the most modern power plants of today that has spurred research efforts into fuel cell development.

The fuel cell differs from the ordinary dry cell or storage battery in that the electrodes are not consumed. The fuel and oxidant are supplied to the cell continuously during its operation and react at their respective electrodes to produce electricity. Modern fuel cells use gaseous fuels, either H_2 or CO or mixtures of these gases. The oxidizer is normally oxygen or air.

The principles of the fuel cell can be demonstrated by using a relatively simple, unpressurized cell which works at room temperature, using methyl alcohol as a fuel and oxygen from the air as an oxidant. Basically, the cell consists of a fuel electrode and an oxygen electrode. Both are immersed in an electrolyte which is a solution of potassium hydroxide in water. The fuel, methyl alcohol, is mixed with the potassium hydroxide solution. Air is bubbled over the oxygen electrode. The following equations show the reactions:

At the fuel electrode:

$$CH_3OH + 4OH^- \rightarrow HCOOH + 3H_2O + 4 \text{ electrons}$$

At the oxygen electrode:

$$O_2 \text{ (gas)} + 2H_2O + 4 \text{ electrons} \rightarrow 4OH^-$$

Net reaction:

$$O_2 + CH_3OH \rightarrow HCOOH + H_2O$$

Additional information may be obtained by requesting the pamphlet, *How To Make a Demonstration Fuel Cell* from the Esso Research and Engineering Co., P. O. Box 45, Linden, New Jersey. See also reference *7R-6.*

Area 7 References

7R-1. The chemical properties of the methyl group. Journal of Chemical Education, v. 30, No. 1: 22-31. Jan. 1953

7R-2. Covalent bonding and resonance in organic chemistry. Journal of Chemical Education, v. 27, No. 9: 504-510. Sept. 1950

7R-3. Small-scale techniques in the teaching of organic chemistry. Journal of Chemical Education, v. 30, No. 6: 296-301. June 1953

7R-4. Small-scale units for organic identification. Journal of Chemical Education, v. 31, No. 3: 144-148. Mar. 1954

7R-5. Biochemical reactions. Journal of Chemical Education, v. 31, No. 6: 282-290. June 1954

7R-6. Fuel cells. Journal of Chemical Education, v. 36, No. 2: 68-73. Feb. 1959

NOTES

AREA 8

Metals and Metallurgy

8.01. Position of Metals in the Periodic Table

Use the periodic table as a point of reference to illustrate the chemical and physical properties of metals (see pages 334—335). Relate to activities 2.21 and 2.22.

Have pupils locate the metals in the periodic table. Show that metals represent a majority (approximately 75 percent) of the elements. Emphasize that there is no hard and fast line between metals and nonmetals, as shown on many charts, but a more or less gradual transition.

The physical and chemical properties of metals are generally related to one or more of the following:

- Number of protons and neutrons in the nucleus
- Number and completeness of the inner electron orbits
- Probable relative position of shells and subshells
- Atomic and ionic radii
- Number of valence electrons
- Type and strength of bonds

When comparing the properties of metals, it is suggested that data be recorded by the pupils on duplicated adaptations of the periodic table as described in activity 2.22. By adopting this procedure, the teacher may give pupils practice in using reference sources. When the information is pooled and recorded on the duplicated sheets, any possible generalization is immediately obvious. Another possible manner for recording the data is shown below.

THE ALKALI FAMILY

Element	Symbol	at. wt.	at. No.	Electronic Structure	Melting Point	Boiling Point	Density gm/Cm^3	Alkali Chloride	Alkali Hydroxide
Lithium	Li	6.940	3	2-1	186°C	1336°C	0.530	LiCl	LiOH
Sodium	Na	23.00	11	2-8-1	97.5°	880°	.963	NaCl	NaOH
Potassium	K	39.10	19	2-8-8-1	62.3°	760°	.857	KCl	KOH
Rubidium	Rb	85.48	37	2-8-18-8-1	38.5°	700°	1.594	RbCl	RbOH
Cesium	Cs	132.9	55	2-8-18-18-8-1	28.5°	670°	1.992	CsCl	CsOH
Francium	Fr	(223)	87	2-8-18-32-18-8-1	Francium has been obtained only in minute quantities as the result of an alpha disintegration of actinium.				

8.02. Metallic Luster

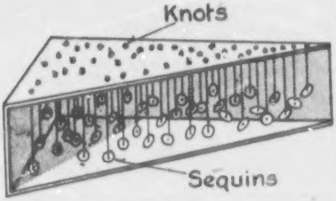
Metals possess certain physical properties which are due to the metallic lattices of their crystalline forms. Recall the lattice structure of crystals and the type of bonding which occurs in the structure.

The metallic lattice may be considered to consist of a definite arrangement of positive ions and a cloud of valence electrons. Although the electrons are free to drift throughout the lattice, the crystal is held together by the attractive force between the positive ions and the electron cloud.

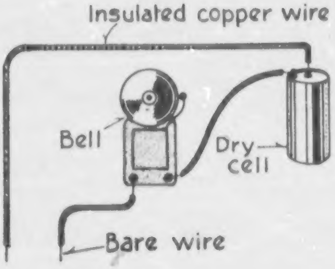
Mobile electrons in the lattice are responsible for the luster which metals display. As light strikes the surface of a metal, it probably affects the electron cloud and causes the electrons to emit visible electromagnetic radiations. The net result seems to be that the electrons reflect back the light which causes a luster. Nonmetals may "reflect" light in a similar manner, but only to a slight degree.

a. Display samples of common metals such as aluminum foil, copper, zinc, tin, iron, silver (coin) and gold foil. Ask pupils to determine what common property the samples have.

b. Cut diagonally across a closed box, such as a shoe box. By means of fine thread of varying lengths hang several dozen mirror-like sequins from the top of the box. Rock the box to get the sequin electrons "drifting," and shine the beam from a flashlight into the box. Note how the light is reflected (see diagram 8.02*b*). Compare the results with the way a metal obtains its luster.



8.02 b



8.04 a

c. Demonstrate the silvery appearance of freshly cut sodium and potassium as examples of uncommon and active metals. Ask the pupils to propose an hypothesis to explain why the luster disappears.

8.03. Malleability and Ductility of Metals

The forces within a lattice determine the malleability and ductility of a metal. If the principal force is uniform in all directions, the positive ion can be transferred from one lattice site to another easily, thus changing the shape of the metal. Essentially, the uniform force is that between the positive ion and the electron cloud within the lattice.

When covalent bonding occurs and causes strong directed forces to exist between adjacent positive ions, there no longer is a uniform force in all directions. The metal tends to be brittle rather than malleable. Metals of Group I*A* are good examples of metals showing malleability. Many of the transition elements tend to be brittle.

a. **Malleability of Copper.** Demonstrate the malleability of copper. With a ball peen hammer pound a sheet of light-gauge copper into an ashtray. The wooden form for ashtrays is usually available from the art department or school shop.

b. **Malleability of Lead.** With a ball peen hammer pound a lead fishing sinker into a "sheet."

c. **Ductility of Metals.** Illustrate ductility by passing around wires of different gauges and composition.

d. **Changing Ductility by Heating.** Bend a bobby pin back and forth several times to show its ductility. It is difficult to break it by bending and flexing. Heat the pin to redness in the bunsen flame and quench by plunging the pin into cold water. The bobby pin is brittle now and can be broken easily into pieces.

8.04. Conductivity of Metals

The drifting of electrons in the metallic lattices allows metals to conduct electricity. Since the electrons are able to absorb heat energy easily and transmit it from place to place, metals are good conductors of heat. Generally, metals in groups I*A* and I*B* are the best conductors of heat and electricity.

Compare metals with nonmetals with respect to thermal and electrical conductivity. Refer to activity 2.21, generalizations *17* and *18*.

a. Show that metals are generally good conductors of electricity. Connect a bell or buzzer in series with a dry cell and two leads, as shown in diagram 8.04*a*. Demonstrate that the bell will ring only when the circuit is completed.

(1) Place a strip of metal such as aluminum, silver, copper or iron across the leads.

(2) Press the leads into a piece of sodium or potassium metal.

(3) Place the leads in a "puddle" of mercury.

b. Support several strips of metal of equal length such as iron, aluminum, copper and tin, so they may be heated from one end. At the other end of each strip adhere a copper coin by means of a drop of paraffin. Heat the metal. When the paraffin melts, the copper coin drops. Compare the conductivities of the metals.

c. Obtain cooking pots of several different compositions such as copper, iron, aluminum and stainless steel. Place 500 ml. of water at the same temperature in each pot. Compare the times required to heat each volume of water to boiling. Some pupils may wish to produce a bar graph of the results. *Note:* Be sure the cooking pots are clean on the bottom. Consider other uncontrolled factors.

8.05. Tensile Strength

Illustrate the differences in tensile strength between different metals. Use two wires of the same length and diameter (*No. 24* or *28* gauge). Support the wires from one end. Add weights until each breaks. The tensile strength varies directly with the force needed to break the wire, and is a measure of the cohesive force between adjacent molecules over the entire cross-sectional area.

8.06. Differences in Melting Points and Boiling Points of Metals

The differences in the melting points (and boiling points) of metals are related to their atomic structures and to forces between individual atoms. See activity 2.21, generalizations *20*, *21*, *40*, *46* and *47*. A graph of the periodicity of melting points is suggested in activity 2.22.

a. Into a cavity in a block of dry ice pour some mercury. After the mercury has hardened, remove it from the dry ice; and place the solid mercury in a beaker. Observe what happens as the solid mercury warms to room temperature.

b. Obtain two similar porcelain crucibles. Into one place a known weight of tin, into the second an equal weight of lead. Heat the crucibles. Note which metal melts first.

c. Repeat the procedure in *b*, substituting copper or zinc for tin. Check the melting points of the metals to explain the results.

d. Hold a small piece of gallium in the palm of the hand. The body heat will be sufficient to melt the metal (see reference *8R-1*).

8.07. Chemical Properties of Metals

As indicated in activity 8.01 the chemical properties of metals are related to many factors including the composition of the nucleus, the number and arrangement of electrons, and the radii of the atoms and ions of the metals. In discussing metals these are some of the factors used to explain the following:

- Tendency to lend electrons and form positive ions
- Tendency to combine with nonmetals

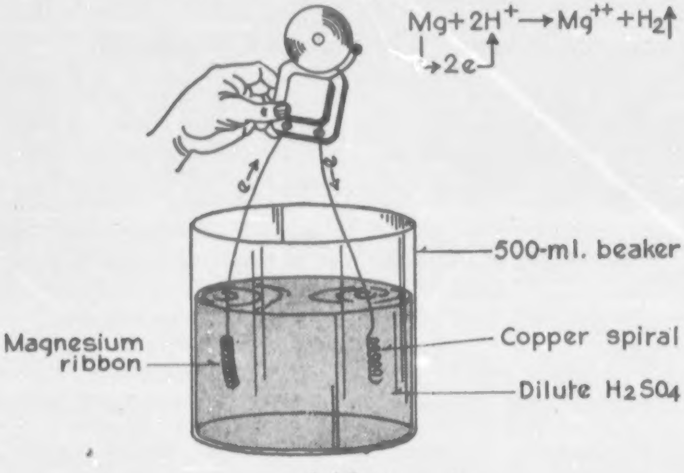
- Tendency to form bases
- Relative activity
- Occurrence of their compounds
- Stability of their compounds
- Energy required to reduce them from their ores

As appropriate in the discussion relate the metals to their positions in the periodic table and to activity 2.21, generalizations *23-29*, *31-34*, *36-38*, *42-45* and *55-64*.

8.08. Metals Form Positive Ions

One of the characteristics of metals is that they tend to lend electrons and form positive ions.

a. Show that metals may produce a flow of electrons which causes a buzzer to ring or an electric lamp to light. Arrange the apparatus as shown in diagram 8.08*a*. Connect a spiral of copper wire to one post of an electric doorbell or buzzer. Bunch together 50 cm. of magnesium ribbon, and attach it to a lead wire by means of an alligator clamp. Fasten the other end of the wire to the second post of the bell. Lower the copper coil and magnesium ribbon into a 250-ml. beaker containing dilute sulfuric acid or hydrochloric acid. A flow of electrons occurs (electric current), and the bell will ring. Similarly, a miniature lamp (1.5 v.) may be substituted for the bell or buzzer. For an alternate demonstration, use zinc in place of magnesium.

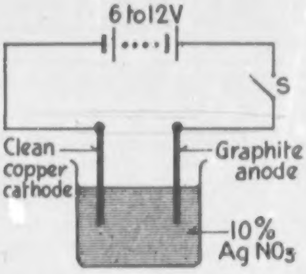


8.08a

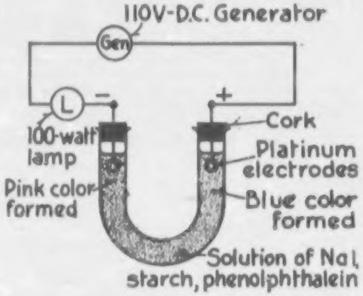
Point out that there is no net gain or loss of electrons in the system. The electrons lost by the magnesium when it is oxidized are gained by the hydrogen ions when they are reduced to hydrogen.

b. The electrolysis of a silver nitrate solution illustrates the tendency of a metal to form positive ions and to be attracted to the negative pole. Dissolve 10 gm. of silver nitrate in 90 ml. of water. Place the solution in an electrolytic cell or beaker. Using a strip of copper as the cathode and a graphite rod as an anode in the beaker, assemble the apparatus as shown in diagram 8.08*b*. Pass a low-voltage (6 to 12 volts), high-amperage direct current through the solution for a few minutes. Silver will deposit on the cathode.

Similarly the electrolysis of copper sulfate solution will produce copper. Use a copper anode and a graphite cathode



8.08b



8.08c

c. Fill a U-tube with a solution containing 10 gm. of sodium iodide, several drops of phenolphthalein and 10 ml. of corn starch solution in about 100 ml. of water. Insert electrodes as shown in diagram 8.08c and electrolyze. If a 110-volt d.c. generator is not available, substitute a 6- to 12-volt d.c. source. If the source of lower voltage is used, the lamp should be removed from the series circuit. If the higher voltage is used, color changes occur more rapidly at the electrodes. A red color at the cathode indicates the formation of sodium hydroxide; a deep blue color at the anode indicates the formation of free iodine.

Although hydrolysis of the sodium iodide causes a faint pink color when the phenolphthalein is added, the color will become more intense as the hydroxide is formed. If a brownish color is observed at the anode, iodine is dissolving in the sodium iodide solution. Increase the amount of starch solution to obtain the blue color.

8.09. Activity Series

a. The electromotive series (activity series) of a group of metals can be experimentally determined by a series of simple experiments using a Daniell cell.

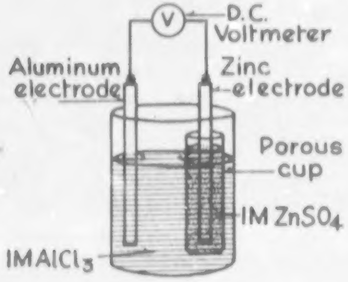
(1) In a Daniell cell, a potential difference (measured in volts) exists between the two electrodes. The magnitude of this potential difference indicates the tendency for the cell reaction to occur. Actually the observed voltage rises from two sources: the voltage at the anode and the voltage at the cathode. Since it is impossible to measure the voltage at either of the electrodes separately, a standard electrode has to be set up. A hydrogen electrode is used as the standard, and its voltage is arbitrarily taken as zero volts. The observed voltage of any Daniell cell with a hydrogen standard electrode is really the voltage of the other electrode. The term oxidation potential is used to describe the latter electrode's voltage.

Although the hydrogen electrode presents too many practical difficulties for the average high school laboratory, the relative electrode potentials of metals can be determined quite easily by the use of a zinc electrode as the reference electrode. The zinc electrode potential is taken at 0.76 volts.

Set up the Daniell cell as shown in diagram 8.09*a*, and measure its e.m.f. by means of a voltmeter. The porous cup, previously soaked in potassium nitrate solution, contains 1M zinc sulfate solution and a zinc electrode. The beaker contains 1M aluminum chloride solution and a strip of aluminum.

Take the reading on the voltmeter. Reverse the connections if the voltmeter needle is not on scale. Theoretically, the reading will be the difference between the electrode potentials of the two metals involved.

(voltmeter reading $=$ electrode potential$_{\mathrm{Al}}$ $-$ electrode potential$_{\mathrm{Zn}}$)



8.09a

Since the electrode potential for aluminum is 1.67 volts and that for zinc is 0.76 volt, the voltmeter reading should be 0.91 volt.

(2) Using the procedures mentioned above, dip the porous cup with the zinc ions and a zinc electrode successively into beakers containing 1M solutions of ferrous sulfate, copper sulfate, silver nitrate and lead nitrate. Each beaker should have the appropriate metal electrode: iron, copper, silver or lead, respectively. Take the voltmeter reading in each case. Be sure to rinse the cup with distilled water before placing it in the next solution. The order in which the metals and their solutions are used above is important insofar as avoiding precipitation is concerned.

If there is difficulty in getting the voltage reading for aluminum, dip the electrode into mercuric chloride solution. The treatment makes the oxide film sufficiently porous so that the true activity of the aluminum becomes manifest.

The teacher may assign part of the work to groups of pupils, each group being responsible for the determination of one metal's oxidation potential.

Arrange the voltage readings with the corresponding metal in decreasing sequence. Note that the sequence corresponds to the order of the same metals in the electromotive force or activity series. Point out that the electromotive series is another name for the list of oxidation potentials.

b. The activity of metals is defined as the ease of losing electrons. The more easily a metal can displace another from its compounds, the more active the displacing metal is. A comparison of the displacing ability of metals provides another method for developing the electromotive or activity series.

Place six test tubes in a rack, and into each pour about 15 ml. of one of the following solutions: sulfuric acid, copper sulfate, silver nitrate, lead nitrate, aluminum sulfate and mercurous nitrate. Place a strip of freshly sandpapered zinc in each solution. Allow the materials to stand for several minutes, and observe whether or not reactions are occurring.

Reactions occur in all cases except that with aluminum sulfate. To determine that a reaction has occurred with the mercurous nitrate, remove the zinc from the solution and rub a finger across it. A shiny deposit of mercury amalgamated with the zinc will be noted. The amalgam is very soft compared with the original zinc. *CAUTION: Be sure to rinse the hands after handling the zinc to avoid mercury poisoning.*

The zinc is found to be more active than hydrogen, copper, silver, lead and mercury; but it is less active than aluminum.

In a similar manner place strips of copper in test tubes containing the salt solutions. Use zinc sulfate in place of copper sulfate.

Place some mercury in a cloth bag, and suspend the bag in a solution of silver nitrate for several hours.

Compare the data obtained from each section of the experiment. List a metal so it is above all metals it can replace from solution.

Check the resulting activity series with the one developed in activity 8.09*a*. A very complete and detailed list is available in chemical handbooks under the topic of "oxidation potentials" or "oxidation-reduction potentials."

c. Compare the lists prepared in activities 8.08*a* and 8.09*b* with the electromotive series shown on page 336. When the list was originally printed, calcium was shown to be above sodium (instead of the reverse as shown in some sources). In response to inquiries, an article entitled "K, Na, Ca or K, Ca, Na?" was prepared by Elbert C. Weaver and Laurence S. Foster. A portion of this article, which first appeared in the 1956 fall issue of *The Science Teachers Bulletin*, is reprinted with permission of the publisher, Science Teachers Association of New York State, Inc.

> The *Reference Tables for Chemistry*, published in January 1956 by The University of the State of New York for use with the Regents Examinations, gives the order *K, Ca, Na.* This order may be contrary to that taught in some New York State schools. But obviously the publication of a list does not settle a question of chemical activity. Let us examine the facts that are behind the list.
>
> ### REPLACEMENT EXPERIMENT MISLEADING
>
> "Why cannot this matter of activity be settled by the usual simple experiment?" you may ask. A number of beakers, each containing dilute sulfuric acid at the same concentration and temperature, are lined up. To them are added in turn small pieces of copper, lead, iron, zinc, magnesium, calcium, sodium and potassium. The increasing rate of evolution of hydrogen from beaker to beaker is a kind of measure of the activity of the metals. An arrangement of these metals in the order in which they seem to liberate hydrogen from dilute acid may be called the *replacement series.* This observation, however, is merely qualitative.
>
> The careful observer noticed during the reaction that potassium (melting point 62.3° C.) and sodium (m. p. 97.5° C.) melted during the reaction, while calcium (m. p. 810° C.) and the other metals did not. In two cases only was the reaction between liquid metals and acid. In all the other cases the solid metals reacted. Furthermore, the metals are not entirely pure, and their surfaces are not uniformly free of oxides and other impurities. The products of the reaction (other than hydrogen) are soluble (as in sodium hydroxide) in some cases, and practically insoluble (as is calcium hydroxide) in others. The heat evolved to form hydrated ions from free ions amounts to 77 kcal/mole for K, 395 for Ca, and 97 for Na, a wide variation.

CONDITIONS MUST BE NOTED

It is well known that the order of chemical activity changes with varying conditions. Ipatieff (Jour. Chem. Educ., 30, 110, 1953) reports the replacement of Cu, Ni, Co, Pb, Bi and Sb as beautiful crystals from their aqueous solutions by hydrogen under pressures ranging from 100 to 600 atmospheres and temperatures from 120° C. to 330° C. Our replacement list now takes on some of the characteristics of the batting order of a baseball team, capable of change at the discretion of the manager.

Suppose that we try to settle the replacement order by an experiment between melted sodium chloride and metallic calcium, and again between melted calcium chloride and metallic sodium. Will Ca replace Na from NaCl or will Na replace Ca from $CaCl_2$? The results of the experiment do not give a clear-cut answer to our questions. In this case, regardless of the melted salt and the elementary metal with which we start, we always end with a mixture of melted NaCl and $CaCl_2$ and a metallic layer containing both metallic Ca and Na. No matter which pair is used at the start, an equilibrium condition is reached.

$$2Na + CaCl_2 \rightleftarrows Ca + 2NaCl$$

A commercial method of producing metallic potassium is to replace it from a fused salt, such as potassium sulfide (K_2S) by sodium, iron, aluminum or magnesium. (C. A. Kraus, Jour. Chem. Educ., 30, 35, 1953).

FREE ENERGY MEASURED

Now let us turn to more fruitful answers. By activity we mean tendency to react. The driving force of a chemical reaction is the "free energy." The reader is referred to *General Chemistry*, Pauling, Freeman, 1956. A simple method to measure free energy is to determine the voltage at 25° C. in a carefully specified voltaic cell. It is customary to use the standard hydrogen electrode as one pole and a half-cell containing the metal as electrode in a solution of its ions as electrolyte as the other pole. The two half-cells are connected by a salt-bridge. The observed voltage of the cell is computed for a solution of metal ions having an activity of one (approximately 1 Normal). This voltage is read as the "standard electrode potential" of the metal, as measured against the hydrogen electrode as standard (with a value of zero). From such an experiment, copper in copper ions shows a voltage of −0.3448 volts, similarly cobalt +0.277, and zinc +0.7620 volts. On this scale the elements potassium, calcium and sodium give values 2.924, 2.87 and 2.714, respectively. The order K, Ca, Na is then established from the standard electrode potential table which is in turn a measure of free energy or of driving force to react. Calcium, then, is slightly more reactive than sodium.

How are electrode potentials determined for such reactive metals as sodium or calcium? The usual experimental method is to use a dilute amalgam of the metal dissolved in mercury. The electrode potential is measured while the amalgam drops from a capillary, thus giving continuously a fresh surface of the amalgam in contact with the solution.

Knowing the standard electrode potentials makes it possible to predict by well known equations what the half-cell values will be under other conditions. R. M. Burns (Jour. Chem. Educ., 30, 318, 1953) has derived a graph which shows the effect of concentration changes on electrode potential. From this graph it is simple to predict the effect of wide changes in the solubility of metal salts on the activity. Such predictions are useful in explaining corrosion of metals.

Professor William T. Hall wrote an article in 1944 on "High School Instruction on the Electromotive Series" (Jour. Chem. Educ., 21, 403, 1944). In this article he explains at greater length the concepts given in this short review. The conclusion is that the experimental facts support the order *K, Ca, Na* that now appears in the *Reference Tables for Chemistry*.

8.10. Metals Combine with Nonmetals

Show that some metals may combine directly with nonmetals by the use of the following exercises.

a. Into a bottle of chlorine gas sprinkle powdered antimony or zinc. Sparks will be seen.

b. Heat a strip of aluminum foil or steel wool in a bunsen burner, and then insert the metal into a bottle of chlorine gas. Combustion will occur immediately. This is an example of an exothermic reaction.

c. Grasp with tongs the end of a short strip of magnesium ribbon and ignite the other end in a bunsen flame. The light emitted contains a high percentage of rays harmful to the eyes. Without looking directly at the ribbon, note that it burns quickly with a brilliant light. Examine the powder formed and compare it with the original metal.

Ask advanced students to "guess" if any product other than magnesium oxide is formed. The nitrogen from the air can react with magnesium at the temperatures produced by the burning. The magnesium nitride appears as a yellowish solid.

d. With tongs insert a wad of steel wool into a burner flame. A vigorous reaction will occur.

Repeat the procedure with a large piece of steel or iron. Ask the pupils to explain why the action was vigorous with steel wool but not with a large piece of iron.

8.11. Metals Unite with Nonmetals in a Definite Proportion by Weight

The law of Definite Proportions can be illustrated with the following exercise.

Weigh 1 gm. of zinc powder and 1 gm. of powdered sulfur. Mix them together on a filter paper by folding the paper back and forth. Pour the mixture on an asbestos square.

Make a second mixture using 2 gm. of zinc and 1 gm. of sulfur, and a third mixture using 3 gm. of zinc and 1 gm. of sulfur.

Set the three mixtures in a row under a hood or other well-ventilated place. *CAUTION: Ignite one after the other with the flame of a burner held at arm's length.* Note which of the above ratios by weight burns the best and has the least free zinc or free sulfur in the product. From the balanced equation of the reaction compute the approximate ratios of zinc to sulfur by weight (see activity 1.18*b*).

8.12. Chemical Properties of Metals

To show that typical metals react with acids to form salts, insert strips of aluminum, zinc, tin and iron into test tubes containing dilute hydrochloric acid. Show that the metals ionize and form salts. Evaporate solutions to dryness to recover the salts.

Repeat the procedure using dilute sulfuric acid. Alert the pupils to observe any difference in the rate with which the metals react with the acid. Formulate a hypothesis to explain why the reaction rates are different. Refer to the electromotive series to test the validity of the hypothesis. Relate to velocity of chemical changes (see activity 9.02).

8.13. Metals Tend To Form Bases

a. Demonstrate that the active metals (see the electromotive series, page 336) replace hydrogen from cool water and that the resulting solutions show basic properties when tested with either litmus or phenolphthalein.

(1) Add a pea-sized piece of calcium to cool water in about 300 ml. of water. Test the solution with an indicator.

(2) *TEACHER DEMONSTRATION ONLY:* Add a small piece of sodium or potassium to a 500-ml. beaker nearly full of cool water. The reaction is vigorous. *CAUTION: Use a pea-sized or smaller particle of the metal to avoid an explosion.* Test the solution with an indicator.

Ask pupils to formulate an hypothesis to explain why the rates of reaction seemed to be different. Check the activity series to test the hypothesis. See the article reprinted in activity 8.09*c* for the explanation of why the more active calcium may react more slowly with water than does the less active sodium. Refer to the *Table of Solubilities* on page 336 and compare the solubilities of $Ca(OH)_2$ and NaOH. Relate to velocity of chemical changes (see activity 9.04*c*).

b. Illustrate the formation of insoluble hydroxides. Refer to the table of solubilities for the solubilities of hydroxides.

(1) Dissolve approximately 1 gm. of ferric chloride in 50 ml. of water. Add a few drops of ammonium hydroxide. The orange-colored flocculent precipitate, ferric hydroxide, is an insoluble hydroxide.

(2) Add some calcium hydroxide (lime water) to a solution of aluminum sulfate. Note the formation of aluminum hydroxide, an insoluble hydroxide.

8.14. Chemical Occurrence of Ores

The ores of most metals contain the metal in the combined or oxidized state. Reduction of the ore is necessary to obtain the metal. The method of reduction used depends upon the activity of the metal and the type of ore in which it is found.

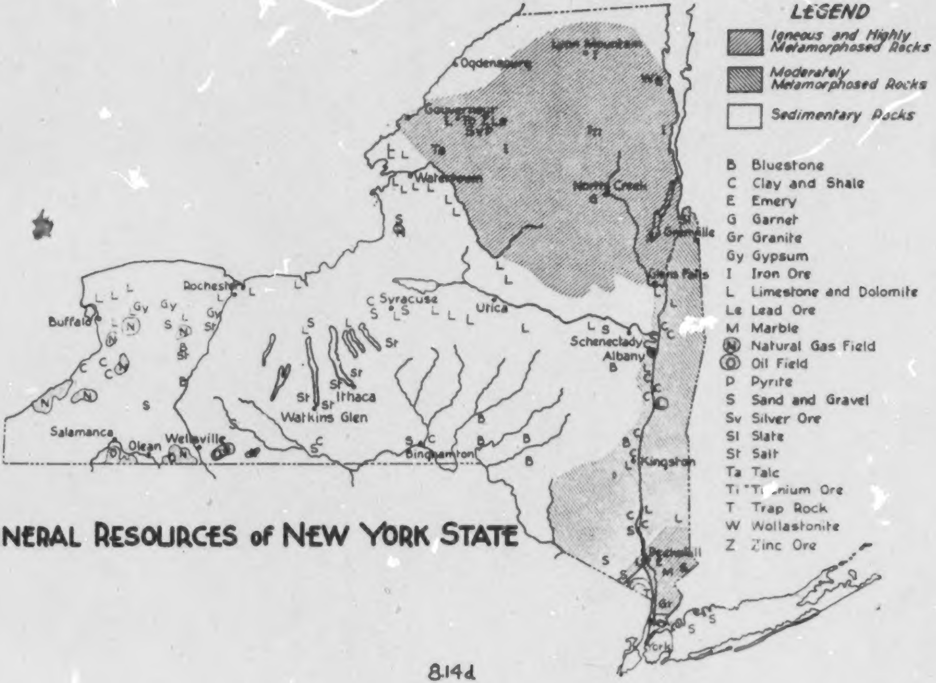
a. Make an exhibit of typical minerals illustrating oxides, sulfides, carbonates, chlorides and sulfates ores. Such an exhibit may contain, among others, specimens of:

Bauxite
Iron pyrites
Galena
Hematite
Magnetite
Malachite
Halite
Fluorite
Carnallite
Siderite
Chalcopyrite
Native copper
Azurite
Sphalerite
Uraninite
Gypsum

b. Plan a field trip to a nearby museum which offers a mineral collection. If previous arrangements have been made, the museum generally offers a special guided tour. (See appendix *C* for suggestions on field trips.)

c. Frequently there is a member of the community who has a rock-collecting hobby. The teacher may arrange to borrow rock specimens or to have a few pupils see the collection and report back to the class. The rock collector may be willing to show his collection and talk with the class at school.

d. New York State has rich ore deposits, the most important of


LEGEND
▨ Igneous and Highly Metamorphosed Rocks
▨ Moderately Metamorphosed Rocks
☐ Sedimentary Rocks
B Bluestone
C Clay and Shale
E Emery
G Garnet
Gr Granite
Gy Gypsum
I Iron Ore
L Limestone and Dolomite
Le Lead Ore
M Marble
Ⓝ Natural Gas Field
Ⓞ Oil Field
P Pyrite
S Sand and Gravel
Sv Silver Ore
Sl Slate
St Salt
Ta Talc
Ti Titanium Ore
T Trap Rock
W Wollastonite
Z Zinc Ore
Ogdensburg
Lyon Mountain
Gouverneur
Watertown
North Creek
Granville
Glens Falls
Rochester
Buffalo
Syracuse
Utica
Schenectady
Albany
Ithaca
Watkins Glen
Salamanca
Olean
Wellsville
Binghamton
Kingston
Peekskill
York

MINERAL RESOURCES of NEW YORK STATE

8.14d

which include those of iron, zinc and titanium. Lead and a small amount of silver are obtained as byproducts of zinc mining. Other important minerals mined in the State are limestone, salt, talc, clay, sand, gravel, garnet and emery. Diagram 8.14*d* shows the distribution of mineral resources in New York State.

8.15. Sources of Metals

Metals are found either in the combined or native state in minerals in the earth's crust (see reference *8R-2*).

a. Refer the pupils to the activity series. Ask them to propose a list of metals which will be difficult to release from their compounds. Likewise ask them to propose a list of metals that may be found uncombined in nature.

b. Use the heats of formation found in a chemical handbook as a means of explaining why it is easier to obtain a metal from one ore than from another.

8.16. Obtaining Active Metals

Active metals may be obtained by the electrolysis of their fused compounds. However, the commercial preparation of many metals involves a method which is cheaper than the electrolytic process.

a. Duplicate a skeleton periodic chart on which only the group and period numbers are marked (see activity 2.22). With a colored pencil have the pupil shade in the area of the periodic chart where the elements obtained by electrolytic reduction are listed. As other general methods of extraction are studied, have the pupil shade in the appropriate sections with colored pencils. Point out that organizing information into large general areas is a rewarding study technique. *Reference 8R-3* presents another organization based upon the periodic chart.

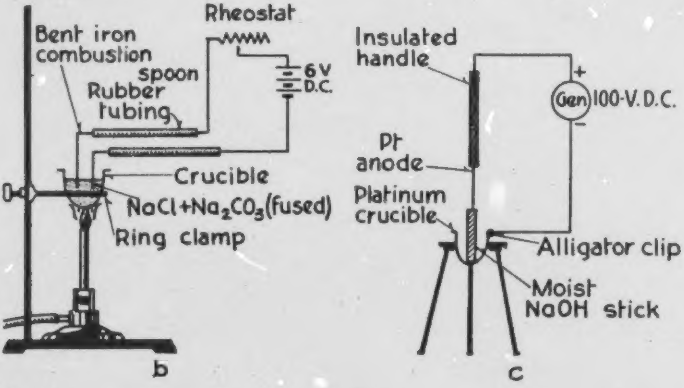
b. TEACHER DEMONSTRATION ONLY: The Downs process can be imitated in the laboratory by using dry sodium chloride mixed with a small amount of sodium carbonate in a clay or platinum crucible (see diagram 8.16*b*). The electrodes are made from iron combustion spoons. They are insulated for holding by means of rubber tubing at the upper ends and bent at right angles about 3 inches from the lower ends so they may be inserted into the fused salt. Connect the electrodes to a 6-volt d.c. source with a variable resistor (rheostat) to control the current. A 6-volt d.c. power supply can be used as the current source and rheostat. To operate the cell, heat the salts until they melt (fuse). Insert the electrodes. Pass the current through the fused salts. When evidence of electrolysis appears, reduce the amount of current;

continue the reaction for several minutes. Allow the salt to solidify before removing the electrodes.

Remove the cathode. Sodium particles become visible upon scraping. *CAUTION: Wear goggles as a protection against spattering. Place the whole cathode in water. The characteristic sodium-water reaction takes place.* Test the water with litmus or phenolphthalein for evidence of a base.

If the cathode is withdrawn from the crucible while it is still hot, the electrode will burst into flame and give the characteristic yellow color of sodium.

The red color at the anode results from the formation of ferric chloride.


Rheostat
Bent iron combustion spoon
Rubber tubing
6 V D.C.
Crucible
NaCl+Na$_2$CO$_3$(fused)
Ring clamp
b
Insulated handle
+
Gen
100-V. D.C.
−
Pt anode
Platinum crucible
Alligator clip
Moist NaOH stick
c

8.16

c. TEACHER DEMONSTRATION ONLY: CAUTION: Wear goggles as a protection against spattering and work under the hood with the door pulled down as far as possible. The Castner method of producing sodium metal can be reproduced in the laboratory. Set up the apparatus as shown in diagram 8.16*c*. Use a platinum wire as an anode, a silver or platinum dish as a cathode and a 100-volt d.c. source of current. Place a stick of sodium hydroxide in the dish, and bring the anode in contact with the upper part of the stick. As the current flows, the sodium hydroxide melts, and silvery globules of sodium appear on the dish. Moistening the stick of sodium hydroxide increases the rate of the reaction.

d. TEACHER DEMONSTRATION ONLY: To obtain calcium or magnesium metal, use the apparatus and procedures given for the Downs process in activity 8.16*b*, substituting calcium or magnesium chloride.

e. Less active metals may be prepared by electrolysis in the laboratory. Use a 6-volt d.c. source and carbon electrodes in each case (see diagram 8.08*b*).

(1) To obtain silver on the carbon cathode, pass a current through a solution of silver nitrate.

(2) To obtain copper use a solution of copper sulfate as the electrolyte.

(3) To obtain lead, tin or mercury, use salt solutions of the metal desired as the electrolyte.

Note: Adding some gelatin to each electrolyte will result in a smoother deposit of the metal on the cathode.

8.17. Extraction of Aluminum

a. Make a display of the materials used in the Hall process for extracting aluminum from its ores. A free demonstration kit containing samples of cryolite, bauxite, alumina and cast aluminum can be obtained, upon request, from the Aluminum Company of America or the Reynolds Company.

b. Refer to any chemistry textbook for a diagram and explanation of the Hall process. Point out that prior to the Hall process aluminum was considered to be more valuable than gold and that it was prepared by reducing the oxide with sodium metal.

8.18. Sacrificial Extractions

Sometimes it is not practical to reduce a moderately active metal in the usual manner with coke. Limited supplies of ores of certain metals and the need for a small amount of metal for a specific job justify the use of a reducing metal that is more costly than coke.

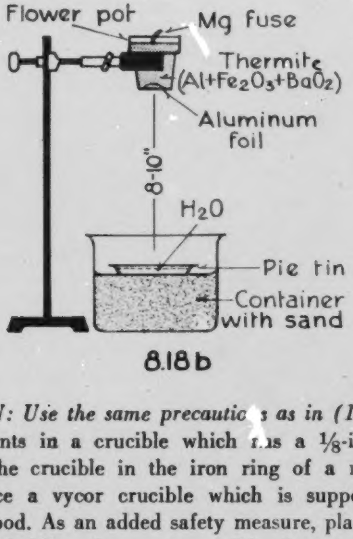
a. Reduction by Magnesium. Bore a small hole in a block of dry ice, and fill it with powdered magnesium. Place a 2-inch length of magnesium ribbon in the powdered metal to act as a fuse. Ignite the magnesium ribbon with the burner flame. After combustion occurs, note the black deposit of carbon around the hole. The magnesium burned by using the oxygen of the carbon dioxide.

b. Reduction of Iron Oxide with Aluminum (the Thermit Reaction). *TEACHER DEMONSTRATION ONLY: CAUTION: Wear goggles and gloves.* The following reaction provides a very spectacular illustration of an exothermic reaction. A darkened room increases the effectiveness of the demonstration.

(1) Place approximately 50 gm. of powdered aluminum and 50 gm. of iron (III) oxide together with 10 gm. of barium peroxide in a

small earthenware flowerpot supported on a ringstand. *CAUTION: Barium peroxide and the thermite mixture may ignite prematurely during the mixing. Use a long stirring rod for the mixing, and stand well back.* Commercial "thermite" mixtures and ignition powder will prove more effective and consistent than the aluminum and iron oxide mixture. The fuse is a 4-inch strip of magnesium ribbon. Place a thin sheet of copper or aluminum over the hole in the bottom of the flowerpot to prevent the mixture from falling through the opening.

About 10 inches below the opening in the flowerpot, place a container with sand on which is resting a small pie tin filled with water or sand (see diagram 8.18*b*). *CAUTION: Stand back.* Ignite the fuse. Molten iron splashes around, runs through the hole in the flowerpot and eats a hole in the pie pan under the water. See references *8R-4-5.*



8.18b

(2) *CAUTION: Use the same precautions as in (1) above.* Put the reacting ingredients in a crucible which has a ⅛-inch hole in the bottom. Mount the crucible in the iron ring of a ringstand. Under the crucible place a vycor crucible which is supported by a clay triangle on a tripod. As an added safety measure, place a pan of sand under the tripod holding the vycor crucible. Ignite the mixture. The molten iron will pour into the vycor crucible which will crack but not break as the iron and slag cool. To remove the glass from the metal-slag material, quench the vycor crucible in cold water.

c. **Reduction of Manganese Ore by Aluminum.** *TEACHER DEMONSTRATION ONLY: CAUTION: Use the same precautions as in activity 8.18b(1). Molten manganese may spatter.* Manganese metal is obtained by reduction with aluminum from manganese dioxide (pyrolusite). The laboratory setup is similar to the thermite reaction.

Equal quantities of powdered manganese dioxide and aluminum are mixed with a small quantity of sodium peroxide as the ignition powder. Magnesium ribbon serves as a fuse.

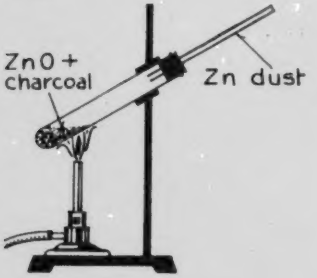
8.19. Reduction with Coke

Moderately active metals are obtained by the reduction of their oxide ores with coke. Pupils can reduce a number of oxide ores in the laboratory.

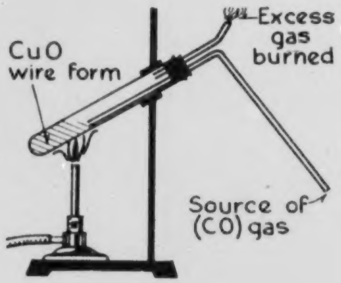
a. **Reduction of Lead Ore.** Place a charcoal block on an asbestos square. With the end of a metal file, dig out a cavity about ¼ inch in diameter. Fill the cavity with about a quarter of a teaspoonful of litharge (lead oxide). Insert a short piece of glass tubing with fire polished ends into one end of a piece of rubber tubing about 1 foot long. Attach the other end of the rubber tube to a blowpipe. Put the glass end of the blowpipe apparatus in the mouth. Hold the blowpipe just above a yellow flame of a bunsen burner, and blow into it. Direct the oxidizing flame on the litharge until small balls of metallic lead appear.

b. **Reduction of Copper Ore.** Mix 2 gm. of copper (II) oxide with 5 gm. of powdered charcoal in a pyrex test tube equipped with a delivery tube leading into a beaker of limewater. Heat the test tube briskly for about five minutes. Empty the test tube into an evaporating dish. Wash away excess charcoal. Bright colored copper is obtained. Identify the other product formed.

c. **Reduction of Zinc Oxide.** Heat a mixture of zinc oxide (zincite) with powdered charcoal or coke in a pyrex test tube equipped with a 10-inch glass tube and a one-hole stopper. Zinc metal, being volatile at the temperature of the reaction, will deposit on the inside of the glass tube in the form of a blue powder (zinc dust). See diagram 8.19*c*.



8.19c



8.20

8.20. The Blast Furnace

In industry iron ore is reduced in the blast furnace. A simplified model of the blast furnace can be constructed and used in teaching the principles of the blast furnace operation. See activity 45 in *Using Chemicals.*

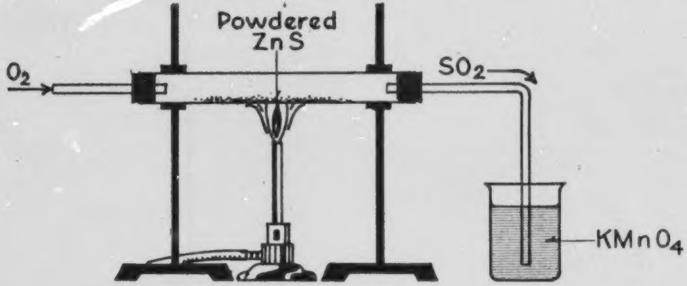
In the blast furnace carbon is first converted to carbon monoxide which is the actual reducing agent. The principle of the reduction of an ore with carbon monoxide is best shown by reducing copper (II) oxide, wire form, with ordinary illuminating gas which contains carbon monoxide. Do not use bottled or natural gas. In diagram 8.20 the pyrex test tube contains the copper oxide. The tube is heated as the reducing agent is passed over the copper oxide. Metallic copper becomes visible within several minutes. Excess gas is burned at the tip as shown.

8.21. Reduction of Sulfide Ores

Before sulfide ores can be reduced with coke, they must be roasted in air and converted into the oxide form:

a. Roasting Copper Sulfide. Place about 10 gm. of copper (II) sulfide in a crucible, and heat strongly with a bunsen burner. Stir the contents from time to time. Note the sharp odor of sulfur dioxide which is produced. Heat for 15 minutes to convert the sulfide to an oxide. Add powdered charcoal and continue heating to reduce the oxide to copper. Lead sulfide may be roasted in a similar manner.

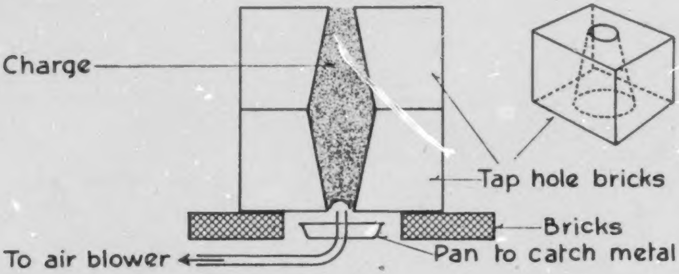
b. Converting Zinc Sulfide to an Oxide. *TEACHER DEMONSTRATION ONLY: CAUTION: Use the hood.* Set up the apparatus as illustrated in diagram 8.21*b*. Pass oxygen either from a generator (or tank) over hot powdered zinc sulfide. The sulfur dioxide gas formed will decolorize the potassium permanganate solution.



8.21 b

c. **Changing Galena to Lead.** A model of a converter used to roast ores can be easily assembled from two tap hole bricks obtained from a local foundry. See diagram 8.21*c.* for setting up the apparatus.

After the converter has been preheated, add a mixture of small pieces of brickettes (compressed charcoal) and powdered galena ore. The flame coming from the top of the converter will change color when the reduction begins. Molten lead will drop out of the lower tap hole.



8.21c

d. **Changing Cinnabar to Mercury.** Put some mercury (II) sulfide or powdered cinnabar ore into a test tube and heat it. Near the mouth of the test tube hold a strip of filter paper which has been wet with potassium permanganate solution. Identify the gas being formed. Continue to heat until all the sulfide is decomposed.

Ask the pupils to explain why carbon is not needed as a reducing agent in this case. Relate to the activity of the metal.

8.22. Roasting Carbonate Ores

The first step in the metallurgy of a carbonate ore is to convert it to an oxide.

a. To show the decomposition of carbonates to the oxide form, heat 10-gm. samples of copper carbonate, lead carbonate and cadmium carbonate in separate crucibles. Use moderate heat and stir occasionally. Continue heating until the change appears to be completed. Add powdered charcoal; continue heating to reduce the oxides to the metals.

b. Heat to decomposition 25 gm. of zinc carbonate in a pyrex test tube. Pass the carbon dioxide gas formed into limewater.

8.23. Metallurgy of Native Ores

Inactive metals are found in the uncombined or native state. They are sometimes found in the sand of stream beds after having been moved by running water from their original rock formation. Native metals are separated from the other materials in the ore by mechanical means. Mining ore of this type requires a modern version of the earlier technique of gold panning (see reference *8R-6*).

a. **Wet Panning.** A mixture of finely powdered galena and fine sand may be used to illustrate the process of wet panning. Place some of this mixture or some Black River sand in a petri dish or pie pan. Hold the dish under a faucet from which a small stream of water is flowing. Tip the dish slightly and swirl the water by moving the dish with a circular motion. Gradually the particles of relatively low density will wash out of the dish. Use a microscope to compare a sample of the original material with the sediment in the bottom of the pan.

Liquids other than water are often used in wet panning. Examples are carbon tetrachloride, acetylene tetrabromide and methylene iodide. The choice of the liquid depends upon its specific gravity relative to those of the ores to be separated.

b. **Concentration of Heavy Ores.** Demonstrate the panning process by using a 10-inch pie tin, crushed gold-bearing ore, an excess of ordinary mud and water. The ore is concentrated by repeated washing under the faucet or tap.

8.24. Amalgamation

Gold and silver are obtained commercially from pulverized washed ore by mixing with mercury. The mercury amalgamates with the gold or silver. The liquid amalgam is separated from the gangue and distilled. The mercury is collected in the receiving container, the native metal in the retort.

Make some silver amalgam by grinding silver foil and mercury together in a mortar.

An alternate method for preparing the amalgam consists of grinding together several moistened silver nitrate crystals and 1 or 2 ml. of mercury in a mortar. It may be necessary to add 1 ml. of water for a complete reaction to occur. The excess mercury dissolves the silver formed by the single replacement reaction. Press the amalgam between several thicknesses of filter paper and let it stand overnight.

Place about ½ gm. of the silver amalgam in a dry test tube and heat it gently. Observe and identify the deposit which appears on the cool part of the test tube. *CAUTION: Do not inhale mercury fumes; they are poisonous.*

8.25. Parks Process

Much gold and silver is obtained from the sludge of the copper refining cells. The metals in the sludge are dissolved in molten lead. About 1 percent of molten zinc is added. Since the native metals are about 3,000 times more soluble in molten zinc than in lead, most of the gold or silver goes into the zinc. The zinc solution rises to the top of the lead and cools to form a solid layer which can be lifted off. The zinc sublimes on heating; the gold or silver is left in the retort.

Use an analogy to illustrate this method. Dissolve some bromine in water; add carbon tetrachloride and shake. Note that the bromine is more soluble in carbon tetrachloride than in water.

8.26. Principles of Concentration of Ores

Concentration of an ore involves the removal of unwanted nonmetallic minerals in order to make the metallurgy of the desired mineral more economical. The process is carried out by a number of methods based upon differences in the properties of the portions of the ore. Substances may be separated if they differ significantly in their:

- Ability to be attracted by a magnet
- Density
- Ability to be wet by water
- Ability to "attract" air bubbles

a. **Separation by Differences in Magnetic Properties.** Prepare a mixture of iron filings and sand. Put a magnet in a plastic bag, and pass the end of the magnet over the mixture. This is the principle used in separating the magnetite (iron) ore of Northern New York State from quartz impurities. Repeat the activity above but put the mixture in a beaker of water. Place the magnet in the beaker. Swirl the beaker. Compare the results of the wet and dry magnetic separation.

b. **Separation by Differences in Density.** Place a piece of coal and a piece of slate in a jar. Fill the jar almost to the top with a saturated zinc chloride solution, and seal the jar. With respect to the solution of zinc chloride, the coal is less dense and floats while the slate is more dense and sinks.

c. **Separation by Differences in Ability To Be Wet by Water.** When a substance can be wet by water, it is said to be *hydrophylic*. However, if it repels water, it is *hydrophobic*. Wool yarn does not wet in ordinary water but will wet if a detergent is added to it.

(1) Fill two large beakers with water. Add detergent to one of them and stir. Pour flowers of sulfur from both hands into the two beakers simultaneously. The sulfur does not penetrate the untreated water and exhibits a hydrophobic surface. In the detergent the surface

of the sulfur is changed to a hydrophylic one, and the sulfur pours like sand into the water.

(2) Add benzene, water and lampblack or powdered charcoal to a beaker. The benzene will wet the charcoal. Both will float on water.

(3) Add carbon disulfide, water and lampblack or powdered charcoal to a beaker. The carbon disulfide will wet the charcoal. In this case the "ore" separates out on the bottom layer.

Note: In these three cases different liquids wet the surfaces. This is the basis for selective adsorption. The density of the wetting agent determines where the ore will be collected.

d. Separation by Differences in Ability To Attract Air Bubbles. The ability to "attract" air bubbles is a variation of the ability of not being wet by water. When air bubbles are attached to ores, the average density of the air and ores is less than the density of the ore. If the average density is less than that of the liquid, the ore and attached bubbles float on the surface.

Fill a test tube about one-quarter full of water. Add sufficient borax crystals to saturate the solution and have some undissolved crystals in the test tube. Stopper the test tube and shake it. Upon standing, the crystals will sink to the bottom of the tube. Add a slight amount of hydrochloric acid. Boric acid crystal surfaces are formed. Again stopper the tube and shake it. Note that air bubbles collect on the surfaces of the crystals.

Boric acid crystals have a nonpolar surface while borax crystals contain unsatisfied bonds or a polar surface. The latter crystals contain strings of $B_4O_7^{-}$ groups, the charge of which is neutralized with hydrated sodium ions. However, the $B_4O_7^{-}$ strings are not neutralized at the crystal surface and hence its polar surface.

8.27. Concentration of Ores by Flotation

Millions of tons of pulverized ore are concentrated by flotation. The process is based upon changing the surface of clean minerals from one wet by water, *hydrophylic,* to one that is water repellent, *hydrophobic.*

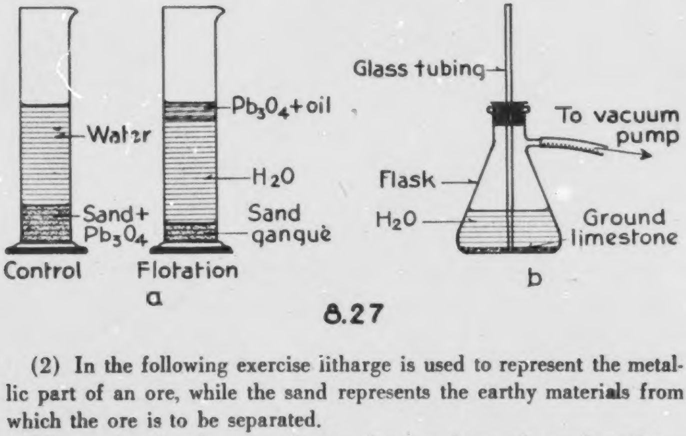
The surface change is brought about by adding to a tank of water containing pulverized ore certain organic chemicals called xanthates which form a molecular film upon the metallic particles only. Often, adding a sudsing agent, such as pine oil, and compressed air creates a froth of air bubbles. The coating on the metallic material attracts the air bubbles. As a result, the air bubbles buoy the ore particles up to the surface. At the top, the froth is scraped off. A desudsing agent allows the metal-bearing materials to be collected.

Sometimes the process is reversed; the quartz is removed in the froth and the metallic particles are left in the water. In this case compounds called alamines and alamacs provide the quartz with a surface that has the affinity for air bubbles.

a. Separation of Ores by Flotation

(1) Demonstrate the separation of an ore from gangue. To a 100-ml. glass cylinder add water, sand (representing gangue) and red lead (Pb_3O_4), which represents the ore. Shake the cylinder briskly; no separation of solids occurs. To an identical cylinder add water, sand and mineral oil. Shake briskly. The oil wets the lead and floats it. The sand sinks to the bottom. See diagram 8.27*a*.

If the contents of the cylinders are stoppered, they can be used without further preparation from year to year.



8.27

(2) In the following exercise litharge is used to represent the metallic part of an ore, while the sand represents the earthy materials from which the ore is to be separated.

Select a bowl and an egg beater that can be used together. Put a mixture of 4 tablespoonfuls of plumbers' litharge and 3 tablespoonfuls of fine white sand into the bowl. Add water to within one or two inches of the top. Place the bowl on several thicknesses of newspaper or set the bowl in a large flat dish. While beating the mixture, add enough detergent to form a thick dense suds. Continue beating; from time to time skim the froth off the surface. Detergent and water can be added as needed. If a small blower is available, the froth may be obtained by blowing air into the mixture of ore, water and detergent.

When the foam does not seem to pick up more litharge, carefully pour off the liquid in the bowl. Inspect the residue. If some of the foam on the paper has not dried so that a residue can be seen, sprinkle alcohol over the suds to break the air bubbles. Compare the composition of the froth's residue with that in the bowl. In industry, silicone polymers are often used as defrothing agents.

Some other detergents may be used. Test the detergent-ore combination to be sure it will allow a thick foam to be formed.

Iron (III) oxide may be substituted for the litharge. Natural ores are not likely to be successfully floated because of the difficulty in pulverization into a fine powder.

b. Flotation of Calcite. Grind a small amount of calcite or limestone as fine as sugar with a mortar and pestle. Put the ground material in a filtering flask. Add water, shake and decant. Repeat until the water is no longer milky. Apply a vacuum to the flask (see diagram 8.27*b*). Note that the air bubbles do not stick to the mineral particles.

Add a small piece of soap to the contents of the flask. Shake the flask. When a vacuum is applied to the flask, bubbles will coat the mineral particles and buoy them up to the surface.

c. Selective Flotation. Ores containing several metals are separated by the flotation process employing different collectors, chemicals which determine the surface to which the air bubbles adhere. Depressors and *pH* regulators play an important part also. The advanced pupil can write to mining industries or do library research to obtain information, and give a report to the class on his findings.

For other ore flotation demonstrations see references *8R-7-9.*

8.28. Separation of Ores by Magnetic Reduction

Taconite ores contain magnetite and hematite. Some magnetite can be removed by magnetic means (see activity 8.26*a*). If the hematite-bearing part is partially reduced with heat in a furnace, the magnetic oxide of iron can be formed.

Use the model of the blast furnace constructed in activity 8.20 to illustrate magnetic reduction. When the furnace is hot, add a mixture of powdered hematite and charcoal. To avoid blowing the ore off the block, add a drop of water to the powder before heating. Keep the air blast at a minimum. After a few minutes shut off the blast. Let the furnace fire go out. Inspection of the contents of the coal furnace will show large chunks of magnetic material.

A similar illustration can be shown by heating with a blowpipe powdered iron (III) oxide on a charcoal block. The residue will become magnetic after several minutes of heating.

8.29. Metals in the Sea

a. For centuries water has been washing against rocks and leaching out some of the mineral content and carrying it to sea. As a result the sea is a treasure chest, a potential source of many metals. Current research is designed to find ways of extracting some of these metals.

It has been estimated that there are 700 ounces of gold in every cubic mile of sea water. As yet, no profitable way of removing it has been found (see reference *8R-10*).

There are deposits of cobalt on the ocean floor. No present mining technique can bring it to the surface.

Ask the pupils to find reports of similar discoveries. See appendix *F* for periodicals that carry such reports.

b. To illustrate the recovery of magnesium from sea water, make some simulated sea water by dissolving as much magnesium chloride and sodium chloride as possible in a liter of water. To this, add 200 ml. of limewater. The magnesium hydroxide will separate out. Filter a small amount of the mixture. The magnesium hydroxide collected on the filter has been extracted from the "sea water." Pour hydrochloric acid on the filter paper to convert the base back to magnesium chloride which is collected as the filtrate.

Point out that, in the industrial process, the solution is evaporated. After being dried and fused, the chloride is decomposed by electrolysis.

8.30. Conservation of Metals

The metals in the earth and the sea are a nonrenewable resource. The use of metals has increased rapidly since 1900. Metals must be conserved and are, to some extent, being conserved by a variety of methods including:

- More efficient mining and metallurgy
- Use of scrap metal
- Substitution of synthetic or other natural materials
- Retarding of corrosion

At appropriate times discuss these methods with any pertinent current examples. Such examples may be found in articles of varying detail in scientific periodicals (see appendix *F*).

8.31. Corrosion

Corrosion is a gradual attack on a metal by its surroundings with the result that the usefulness of the metal is often destroyed. The gases in the air, moisture and chemicals all make a contribution to corrosion.

a. Atmosphere Corrosion

(1) Lay strips of ordinary iron, galvanized iron, tin and aluminum on wet toweling paper. Moisten the toweling as needed over a period of several days, and then inspect the surfaces of the metals.

Note: If the toweling is wet first with dilute acetic acid, the rusting process will be hastened. The acid acts as a catalyst.

(2) Clean three nails by sandpapering them. Do not touch the sandpapered areas with the fingers as the skin can leave a grease film on the metal. Holding the nail with tongs, rinse each nail with distilled water. Place a nail in each of three test tubes. Pour distilled water over one nail, carbonated water over the second and salt water over the third nail. Let the nails stand in their respective liquids for several days. Inspect the nails for evidence of corrosion.

(3) Collect some water from a puddle on a street that has recently been salted to melt snow or ice, or prepare a similar solution using calcium chloride as the solute. Clean two nails as in (2) above. Place one nail in a test tube containing distilled water, the second nail in a test tube containing the salt solution. After a few days inspect the nails for corrosion. Relate the results to corrosion on automobiles.

b. **Corrosion by Direct Chemical Attack.** Corrosion may occur through either direct chemical attack or electrochemical action. Chemical attack involves no microscopic flow of current, and the surface of the metal is fairly uniformly rusted.

(1) **Tarnishing of Silverware.** Place a polished silver spoon in mustard, mayonnaise or a bottle containing a little hydrogen sulfide. After a few minutes inspect the surface, and note the film of tarnish. Point out that the sulfur compounds in air or food can cause the corrosion of silver.

(2) **Action of Distilled Water on Lead.** Place a clean piece of lead in a beaker of distilled water. After a few hours, note the coating of white corrosion products. Point out that lead should not be used in soft, potable water supplies because of the toxicity of corrosion products.

c. **Effect of Temperature on Corrosion.** At high temperatures, steel forms a scaling of corrosion. Review the general principle of increasing a reaction rate by increasing the temperature (see activity 9.03).

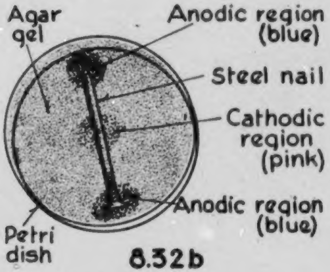
8.32. Corrosion by Electrochemical Action

When two dissimilar metals are connected and immersed in an electrolytic solution, a galvanic cell is formed (see activity 8.09). The metal which is higher in the series tends to be attacked, give up electrons and become the anode. At the other metal electrode, hydrogen or some metallic element is deposited. The original metal of the cathode is protected by the action occuring at the cathode. The rate at which the galvanic attack occurs depends upon the cathode-anode area ratio. A relatively small anode will be attacked much faster than a larger anode will be (see reference *8R-11*).

a. Galvanic Corrosion. Demonstrate the theory of corrosion by placing a strip of zinc and a strip of copper in dilute sulfuric acid, and connect the two metals to the terminals of the galvanometer. Note that the zinc anode is eaten away and that the gas bubbles protect the copper cathode.

Two dissimilar metals in contact with an electrolyte are required for corrosion. Moist air serves as the electrolyte in ordinary corrosion.

b. Anodic and Cathodic Areas on Same Metal. Show that both anodic and cathodic areas may be formed on the same piece of iron in the following manner. Dissolve 2 gm. of agar in 100 ml. of boiling water. Add 1 gm. of sodium chloride, 2 ml. of phenolphthalein and 5 ml. of 1 percent potassium ferricyanide to the solution. Pour a layer of this agar mixture into a petri dish, and allow it to solidify. Press into the agar layer a piece of iron or steel such as a nail, screw or washer. Cover the object with another layer of warm agar solution (see diagram 8.32*b*).



8.32b

After a few minutes a blue color (Turnbull's blue) appears in the gel at the anodic region or regions where the iron is dissolving. A pink color indicates the cathodic region. The effect becomes more distinct with time. Stresses and strains as produced by hammering will produce anodic and cathodic areas in the same piece of metal.

Note: The mixture is more sensitive if the initial *pH* is adjusted to 8 with dilute sodium hydroxide solution. The reaction is faster if a little sodium chloride is added to increase the conductivity.

c. Electrocouple Action. Prepare an iron-aluminum couple by fastening clean strips of the two metals together with a rubber band. In a similar way prepare an iron-copper couple.

Half fill three 250-ml. beakers with distilled water. Add a few drops of potassium ferricyanide solution to each beaker. The chemical will serve as an indicator to show the presence of the Fe^{++} ion.

Place the Fe-Al couple in the first beaker, the Fe-Cu couple in the second beaker and a clean iron strip in the third beaker.

Account for the appearance of the blue color only in the beaker containing the Fe-Cu couple. Relate to the activity series.

d. **Local Action.** Place a strip of chemically pure zinc in hydrochloric acid diluted with distilled water. No action occurs. Now touch the zinc with a platinum or copper wire which has also been placed in the solution. Immediately, gas bubbles appear on the surface of the platinum, and the zinc starts to go into solution. The zinc in this case is the anode of the cell. Next touch the zinc with a strip of magnesium ribbon. The gas bubbles now appear on the less active or cathodic zinc. Commercial zinc will react with the acid because such zinc contains dissolved carbon particles which act as cathodic areas.

This demonstration is very effective if performed in a petri dish and projected on a screen by an overhead projector (see appendix *B-1*).

See references *8R-12-13* for information describing corrosion of aluminum due to impurities.

8.33. Corrosion-Resistant Coatings

Both from the standpoint of conservation and economy it is important to prevent corrosion. One preventative measure is to seal the surface with a film which can not be penetrated by corrosive agents. Some examples are:

- Paints and varnishes
- Waxes and grease
- Vinyl-coated steel and a plastic-laminated steel surface (see references *8R-14-15)*
- Resins, tar, asphalt compounds, adhesive tape and plastic tapes
- Ceramic materials such as fired enamelware (see references *8R-16-18)*

a. **Painting To Prevent Corrosion of Metals.** Clean the surface of a piece of scrap iron with sandpaper. Paint one end of the iron. When the painted portion has dried, dip the entire piece of metal in water. Hang the metal in air for a few days. Then examine all the surface of the iron for rust.

b. **Purpose of Oils Used in Paints.** Obtain four pieces of scrap metal and label them *1, 2, 3* and *4*. Brush several coats of mineral oil on number *1*, of tung oil on number *2*, of boiled linseed oil on number *3* and of motor oil on number *4*. Wash the brushes in kerosene. Hang the pieces of metal in air for several days. Inspect the oily surfaces daily, and keep a record of any changes in the oiled surfaces.

Some of the oils will oxidize and harden to form a rubberlike protective coating. Oils which harden to form a protective film are the "vehicles," the main constituents in some paints. A drier that acts as a catalyst to speed the oxidation of the oil and a coloring pigment are the other ingredients of oil paint.

8.34. Forms of Corrosion

Pupils may be interested in knowing more about the way in which corrosion can occur.

- Pitting results from the formation of small holes which may penetrate thin metals. It is caused by electrochemical attack. Automobile trim experiences pitting.
- Intergranular attack produces cracks in the metal. Electrochemical action is the cause.
- High-temperature corrosion produces flaking. This type of corrosion is a problem in high-temperature engines and jets.
- Erosion-corrosion occurs when mechanical means remove a passivity layer. The flow of gritty liquids over the surface often is the means of removing the surface layer.
- Cavitation often accompanies erosion-corrosion caused by turbulent liquids. The metal develops small cavities.

8.35. Passivation

If a metal reacts with a corroding agent to form a sealing film which inhibits further attack on the metal, passivation is said to occur.

Most passive layers are oxides, although some are carbonates and sulfates. The surface on aluminum is an oxide; the surface on stainless steel is probably an oxide.

a. Passivity of Aluminum. Show that the reaction of aluminum with dilute hydrochloric acid is slight in spite of the relatively high position of aluminum in the electromotive force series. This passivity of aluminum is due to the natural coating of oxide which the metal normally holds.

Clean a strip of aluminum with steel wool. Dip the strip into mercury (II) chloride solution for a few seconds. Now immerse the aluminum in water or dilute HCl. The clean aluminum is now active enough to replace hydrogen from water or acid.

Dry the aluminum with a towel, and expose it to the air. The aluminum oxidizes very rapidly. Observe the heat produced by this oxidation by holding the aluminum in your hand. Relate to activities 9.02 and 9.04.

Further information can be found in references *8R-12* and *19.*

b. Making Iron Nonreactive. Iron can be made nonreactive by the action of certain oxidizing agents. Dip a clean iron nail into concentrated nitric acid and then into a solution of 1:1 nitric acid. It becomes coated with an oxide which resists corrosion. Demonstrate that the nail resists corrosion by:

(1) Rinsing it with distilled water and dipping it into dilute hydrochloric acid. Note that hydrogen is *not* released.

(2) Dipping it into a copper sulfate solution. It will not become coated with copper.

(3) Destroying the passivity of the iron by filing a notch into the oxide coating. Then dip into hydrochloric acid or copper sulfate solution and note reactions.

c. Coating with Other Metals. Metallic coatings are often used to prevent corrosion of the base metal. The coating must have the passivity property. Electroplating, dipping and spraying with atomized molten metal are some of the ways to put on the coating (see references *8R-20-21).*

(1) **Electroplating.** Objects to be electroplated must be chemically clean. Clean each one with steel wool and then bathe it in a hot solution of washing soda to remove any grease. Wash the object in dilute sulfuric acid to remove any oxide coating. The object to be plated is the *cathode* of the apparatus while the plating metal is the *anode.* Use a direct current of from 3 to 6 volts. The electrolyte is a saturated solution of a salt of the metal to be plated. Add a small quantity of gelatin to the electrolytic bath to produce a smoother deposit.

- *Copper Plating*—The electrolyte may be a solution of copper sulfate.
- *Nickel Plating*—The electrolyte may be a solution of nickel ammonium sulfate to which is added a small quantity of ammonium chloride, boric acid and gelatin.
- *Chromium Plating*—First plate the object with nickel. Then use a solution of chromic acid (chromium oxide) as the electrolyte.
- *Cobalt Plating*—The electrolyte may be a solution of cobalt chloride.
- *Silver Plating*—The electrolyte may be a solution of silver nitrate.

(2) **Galvanizing.** Clean an iron object such as a nail by dipping it into dilute hydrochloric acid and then washing it with water. Melt some zinc in a crucible. Dip the iron object into the molten metal.

8.36. Cathodic Protection against Electrochemical Corrosion

Expendable anodes of zinc or aluminum can be used in situations where galvanic corrosion occurs. The zinc or aluminum makes the corrodible metal change to a cathode.

a. Place in three separate 250-ml. beakers, each containing 100 ml. of distilled water and several drops of phenolphthalein, a (1) clean strip of magnesium, (2) clean strip of iron and (3) couple made by winding a strip of magnesium ribbon about a strip of iron. In the third beaker a pink color develops as the more active or anodic magnesium goes into solution. The other two beakers act as controls.

b. To each of three electrolytic cells connect one dry cell in series. Use a saline solution (½ gm. of NaCl per liter of solution) as the electrolyte. For each cell use a 4-inch × 1-inch iron strip fitted with an electrical connection and a graphite rod as the electrodes. In this exercise the formation of the red-brown iron (III) hydroxide is used as evidence of corrosion.

Immerse the two electrodes in the first cell (the control) but do not connect to the dry cell. A moderate amount of corrosion occurs.

In the second cell connect the electrodes to one dry cell. Make the iron anodic. A larger amount of iron (III) hydroxide forms, showing that the process of corrosion has been increased.

Connect the third cell as above but make the iron cathodic. A relatively slight deposit of iron (III) hydroxide forms. The current from the single dry cell opposes electrolytic corrosion.

This demonstration may be expanded by varying the applied voltage or substituting aluminum and other metals for iron.

The principle of cathodic protection is applied to underground structures such as pipelines, sheathing on cables and storage tanks. Instead of a generator to supply the balancing current, zinc electrodes are attached to the lines, cables or tanks and driven into the ground. The zinc becomes anodic.

Many household hot-water heaters are equipped with expendable magnesium or zinc rods in the tank to protect the exposed steel. Ships' hulls often have zinc or magnesium blocks attached in the vicinity of the brass screws.

8.37. Metallurgy of Iron

The presence of small amounts of impurities in a metal alters the properties of the metal. The process used for removal of the impurity depends upon the base metal as well as the kinds of impurities.

Processes used in the metallurgy of iron are excellent examples of principles learned in other areas of the chemistry course.

a. Removing Carbon from Cast Iron. Review the reducing ability of carbon. Note that the iron oxides of rusty scrap steel in the charge of the open hearth furnace are not only used to reclaim the iron but also to reduce the carbon content. Iron ore is another source of oxygen. Bessemer converters use blasts of air to remove carbon. Indicate why the open hearth method is more widely used.

The turbo-hearth furnace combines the principles of the open hearth furnace and the Bessemer converter (see references *8R-12 and 22*).

b. Removing Sand and Phosphorus. Discuss the relationship between the composition of the charge and that of the impurity.

c. Removing Oxygen. After the steel has been removed from the furnace or converter, there is still some oxygen left. To prevent undesirable properties caused by the presence of oxygen, materials called oxygen scavengers are added.

Illustrate an oxygen scavenger at work. Sandpaper a piece of aluminum, and note how quickly the surface dulls as the metal reacts with oxygen. Discuss other metals or minerals that can be added to steel to remove oxygen.

8.38. Treatment of Steels

There are numerous ways of handling steel and changing its properties by mechanical or heat treatment.

Obtain three razor blades of the blue or violet steel type. Keep one blade as a control. Heat the other two blades for a short time in a burner or on the plate of an electric heater. Quench one blade in very cold water. Allow the other to cool in air. Carefully scrape a little of the oxide off the blades. Compare the appearance of the heated and control blades.

CAUTION: Steel particles may fly. Work under a hood with the door open only far enough to insert the hands and equipment. With tongs in each hand, grasp the ends of the control blade. Bend the blade so the ends come together. Repeat the process with the heated blades. Compare the ease with which the blades bend, break or shatter.

Refer superior students to the bibliography for a report on changes in structures and stresses as a result of heating.

8.39. Powder Metallurgy

a. Improving hardness of metals can be accomplished by controlling grain size. A recent method uses metallic powder. The powdered metal is subject to intense pressure as the metal is put into a mold. Heating the metal causes changes in density. Among the numerous sources reporting progress in powder metallurgy are references *8R-23-28.* Alert pupils to watch for progress in the field.

b. The method by which the metal powder is made determines its use. An interesting project for the more advanced student might deal with the production of metallic powders.

8.40. Refining of Copper

Copper ores generally contain zinc- and lead-bearing minerals. Although the copper concentrate is removed by flotation, some of the other metallic minerals are carried along with the copper. These metallurgical processes do not remove all the metallic impurities of gold, zinc, silver and lead. An electrolytic refining process is needed.

a. Into a copper sulfate solution place a carbon anode and a graphite cathode. Connect the electrodes to a d.c. source. After a few minutes, note the deposit on the graphite pole. Use electronic equations to explain why the copper was deposited.

b. Add some clay to a saturated copper sulfate solution. Connect two strips of copper to a d.c. voltage source, and place the strips in the clay-copper sulfate mixture. Six volts are sufficient, but the operation is more rapid with higher voltages. The strip connected to the anode decreases in weight while the copper plates on the cathode. The clay represents the sludge that forms by the disintegration of the blister copper at the anode.

Refer to the oxidation potentials of the metals to explain why proper voltage control assures the depositing of copper only.

8.41. Zone Refining

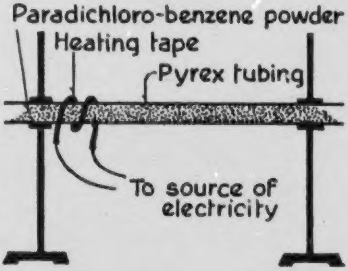
A recent technique that has been developed to purify the materials needed for transistors and solar batteries is zone refining. A heating coil is moved slowly along a column of impure material. In the area beneath the coil, the material to be purified melts. As the coil moves along the tube of material, the resulting liquid slowly recrystallizes to the basic material. The impurities tend to stay dissolved in the melted zone. Thus, the recrystallized material has been freed from some impurities. Repeated zone meltings can produce a higher degree of purity. Silicon, germanium, arsenic, niobium and boron are among the materials refined by zone melting.

Obtain a foot or two of pyrex glass tubing, 10 mm. in diameter. Fill the tube with powder obtained by grinding colored paradichlorobenzene moth cakes in a mortar. Support the tube on the ends, and near one end wrap heating tape once or twice around the tubing to make a heating coil. Connect the tape to the recommended electric source (see diagram 8.41). Manually advance the heating coil about

½ inch every half-hour. A color change indicates a change in the concentration of impurities in the crystals.

Note: Best results will be obtained if a constant gradual movement of the molten zone is obtained by using a clock mechanism.

Additional demonstrations on zone refining can be found in reference *8R-29.*



8.41

8.42. Alloying

A combination consisting of a metal and one or more other elements and having metallic properties is called an *alloy.*

a. **Composition of an Alloy.** Point out that the components of any alloy may be in the homogeneous or heterogeneous condition. An alloy may:

- Be a solid solution containing only one type of crystals. In a random manner atoms of one element fit into some of the lattice sites in the crystal structure of the second element. Sterling silver and brass are two examples of solid solutions.
- Contain compounds. Examples are carbon steels containing Fe_3C, and bearing steel containing SbSn and Cu_3Sn.
- Contain crystals of two or more different elements or compounds. Alloys of bismuth and cadmium contain tiny crystals of each metal.

b. **Special Properties of Alloys.** Combining and mixing different metals in varying proportions can produce special properties. However, the properties of an alloy cannot be predicted from the known properties of its constituents. In the case of many metals, the addition of:

- Carbon to iron increases the brittleness

- Aluminum, manganese, magnesium and chromium increases the resistance to corrosion
- Copper increases the hardness
- Bismuth decreases the melting point

Demonstrate how the hardness of a metal may be increased by adding another metal having atoms of a different size.

Completely fill the bottom of a small box with rows of equally sized marbles. Place a few incomplete rows of the same kind of marbles in the second tier. With the eraser end of a pencil, push against the top row(s). Note how easily dislocations appear.

Replace one or two marbles in each row of the bottom layer with larger marbles. Repeat the above procedures. Try substituting in the bottom row a few marbles smaller than the original ones. Compare the ease with which atoms in the second row can now undergo dislocation. Relate to the addition of copper in silver or aluminum alloys.

c. Making Some Alloys. The general method for making an alloy consists of dissolving small pieces of the various metals into the metal with the lowest melting point. The metals are placed in a crucible and heated. A small amount of anhydrous sodium carbonate is used to prevent oxidation of the metals during heating. The carbonate can easily be skimmed off if the alloy is cast into a mold.

(1) Wood's Metal. Melt together 4 parts of bismuth, 2 parts of lead, 1 part of tin and 1 part of cadmium. When fused, pour the alloy into water to solidify. The Wood's metal solidifies at about 65°C. Save the Wood's metal. It can be used from year to year. Place some melted Wood's metal in a plaster of paris mold in the shape of a spoon. After the alloy has solidified, have a pupil stir some boiling water with the spoon. The effect upon him and his classmates is startling.

As a class project make samples of Wood's metal using different ratios than the one listed above. Compare the melting temperature of the samples made.

Place the alloy in a beaker containing some water. Insert a thermometer in the water. Heat the water until the alloy melts. While stirring, slowly add cold water to the beaker until the alloy solidifies. Record the temperature at which the metal solidifies. It is also the melting temperature. Additional techniques for determining melting points may be found in organic chemistry laboratory manuals.

(2) Solder. Melt together equal parts of lead and tin. Pour this into a greased cardboard mold such as a match box to solidify. Use the solder to join two pieces of iron wire.

An interesting pupil project is the study of different kinds of solders.

Consider the melting temperature of each type of solder and the kinds of metals the solder will join. Some solders contain a flux core to clean the surfaces to be joined so that the solder can adhere. Find out the types of fluxes used and the conditions under which they can be used.

(3) **Rose's Metal.** Melt together 11 parts of lead, 2 parts of bismuth and 1 part of tin. Because of its low melting point, this alloy can be used for electric fuses, as well as safety plugs for boilers and automatic sprinkler systems.

(4) **Amalgamation.** Dissolve 4 gm. of copper sulfate in 10 ml. of hot water. Add the hot solution to about 1 ml. of mercury in a mortar. While grinding, add 4 gm. of zinc dust. The amalgam should become very pasty and then solid. If the amalgam does not harden, grind more zinc and copper sulfate crystals into the solution in the mortar. Drain off the liquid in the mortar, wash the amalgam under the running water, and dry it between pieces of filter paper.

Relate to single replacement reactions. The copper is formed by the reaction between zinc and copper sulfate:

$$Zn + CuSO_4 \rightarrow Cu + ZnSO_4$$

The copper and some zinc dissolve in the mercury. The resulting alloy is an amalgam containing zinc, copper and mercury.

d. **Development of New Alloys.** Current information on this topic may be found in scientific periodicals (see appendix *F*). One example is a preliminary study which indicates the possibility that iron-manganese-aluminum alloys may replace the strategic stockpile minerals, chromium and nickel. Other alloys are needed which can resist the temperature changes in missiles. See also reference *8R-30.*

8.43. The Changing Importance of Metals

The changing needs of society and the depletion of ores change the demand for certain metals and may lead to the development of new metallurgical techniques. Current information on these changes can best be found in scientific periodicals (see appendix *F*). Following are examples of information obtained from various periodicals.

a. New Metallurgical Techniques

- Ion exchange separation has made it possible to obtain rare earth metals and their oxides. They are being used as oxygen scavengers in steel making, sources of X-rays and getters for vacuum pumps (see reference *8R-31*).
- Melting techniques using vacuum degassing are used in the production of better and more dependable alloys (see reference *8R-32*).

- Jet cooling can be used to reduce the time for an annealing process from 120 hours to 30 minutes (see reference *8R-33*).
- Beryllium, a very light metal, has presented many problems in its metallurgical processes. A method has been found to reduce the brittleness of beryllium (see reference *8R-34*).
- Fiber metallurgy is a new development in the use of metallic powders (see references *8R-23 and 25*).
- Scientists may have found a cheap method of extracting titanium by a new electrolytic process (see reference *8R-38*).
- New coatings for metals allow them to be used in different ways. See reference *8R-16* for a description of ceramic coatings for missiles. See reference *8R-36* for information concerning the metals used in the Vanguard satellite.

b. **Metals of Increased Importance**

- Nuclear energy applications have changed uranium from a laboratory curiosity to an important metal (see reference *8R-37* and the bibliography).
- Zirconium has been established to be the toughest metal available for atomic reactors while hafnium is superior to boron and cadmium for use in control rods (see references *8R-38-39*).
- Titanium has many desirable properties such as resistance to corrosion and an ability to withstand heat. It has the strength—but only half the weight—of steel. Unfortunately, its extraction from the abundant ore sources is costly. The use of titanium and its alloys will probably increase as production costs go down (see references *8R-30-35 and 40*). See also the bibliography for additional information about metals which have come to the foreground in importance.

8.44. Spectroscopy

When a beam of sunlight is passed through a prism, the complete rainbow with one color blending into the next color can be seen on a screen or wall. This rainbow is called a continuous spectrum. When a salt is vaporized in a flame, the flame becomes colored. If this light is passed through a prism, narrow bands of color are seen. A line spectrum rather than a continuous spectrum is formed.

When a salt is heated in a flame, electrons in the atoms are raised to higher energy levels. As these electrons drop back to lower energy levels, they emit light. When this light is passed through a prism, a line spectrum characteristic of the material is obtained.

Spectroscopy is a method of analyzing the energy values of light emitted by vaporized materials. Each element has its own identifying color lines in the line spectrum.

a. **Flame Tests.** Some vaporized materials give off a limited set of wave frequencies (colors) to which the eye is sensitive. A crude spectroscopic analysis can be made by identifying the color of the flame in which a material is being vaporized.

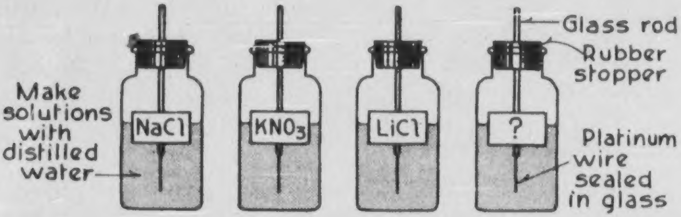
(1) Clean a platinum wire by dipping it in concentrated hydrochloric acid. Hold the wet wire in the flame. Repeat the dipping and heating processes until the platinum wire does not impart any noticeable change in the color of the burner flame.

Dip the clean wire into a solution of barium chloride. Place the wire in the flame, and note the color that appears. Repeat the procedure using salts of lithium, sodium, calcium, copper, strontium and potassium. Refer the pupils to the flame test reference chart found on the reference tables (page 336) to confirm their results.

A convenient means of flame testing consists in preparing a series of flasks or bottles as shown in diagram 8.44*a*. Fit a small bottle with a 1-hole stopper through which extends a glass rod. A platinum wire sealed into the lower end of the rod dips into the salt solution to be tested. When in use, the rubber stopper becomes a handle. Place the platinum wire with its salt solution in the burner flame. Then return the wire to the proper bottle.

(2) The flame tests may be demonstrated rapidly.

Fill salt cellars with salts of metals. Shake the salt into the flame.

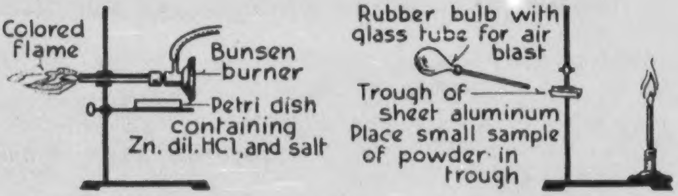

Glass rod
Rubber stopper
Make solutions with distilled water
NaCl
KNO3
LiCl
?
Platinum wire sealed in glass

8.44a

Mix samples of the salts to be tested with alcohol and a small amount of sulfuric acid. Place the sample of each salt and its alcohol mixture into separate evaporating dishes, and ignite the liquid.

Place a sample of each of the salts to be tested in a separate petri dish containing zinc and dilute HCl. Set up the apparatus as shown in diagram 8.44*b*.

Blow powdered salts directly into the flame as shown in diagram 8.44c.


Colored flame
Bunsen burner
Petri dish containing Zn. dil.HCl, and salt
Rubber bulb with glass tube for air blast
Trough of sheet aluminum
Place small sample of powder in trough

. b 8.44 c

(3) Show how blue glass is used to filter out the interference of sodium traces from the potassium flame. View the burner flame through a square of cobalt glass or a blue gelatin spotlight filter. The yellow flame of sodium salts is not allowed to pass through the filter; however, the violet flame of potassium can be seen.

b. Making and Using a Simple Spectroscope. At the end of a board about 8 to 10 cm. wide and 60 cm. long place a lump of modeling clay. Press two razor blades into the clay so that their sharp edges are perpendicular to the board and form a slit no wider than 1 mm. At a distance of 50 cm. from the slit, erect a plastic replica diffraction grating. (An inexpensive grating slide can be obtained from optical or scientific supply houses.) To support the grating, use another piece of clay; or set into the board four nails so that there are two nails on either side of each vertical edge of the slide.

When the spectroscope is to be used, support it at eye level. The room must be as dark as possible. Place the light source to be analyzed about 30 cm. behind the razor blade slit. Look through the grating slide toward the light coming through the slit. Move the head, so that the eye can scan the area to the right and left of the slit.

If too much light comes from the light source, the spectrum may not be visible. Then, it is necessary to erect a screen around the source to allow only a part of the light to enter the slit. If the light produces a fuzzy spectrum, the slit size must be adjusted by moving the razor blades closer together.

Although the flame tests can be observed through the spectroscope made in this activity, best results are obtained by using spectrum tubes. Mount the spectrum tube between the high-voltage terminals of an induction coil (refer to activity 2.17).

Some Geissler tubes may also produce line spectra that can be observed through this spectroscope.

c. **Importance of Spectroscopy.** A large percentage of all analysis is done today by means of spectroscopes. Present the following for class discussion:

- The method is a speedy one. For example, within three minutes from the time a sample of molten steel is taken from the furnace, its exact composition can be spectrographically determined (see reference *8R-41*).
- The molecular architecture of organic compounds can be determined. When infrared light is passed through organic materials, discrete energy values are transmitted or absorbed. By evaluating the frequencies transmitted, different carbon groups and chains can be identified. In making synthetic drugs such as penicillin, infrared spectroscopy tells the chemist when he has made an exact replica of a natural complex molecule.
- Because of its speed and accuracy, spectroscopy has made almost all the other analytical methods secondary in importance. The latter methods are used only when so little analysis is done that it is cheaper to pay for the time-consuming chemical methods than to invest several thousand dollars in the spectrographic instruments.

8.45. Sulfide Tests

A number of metals may be precipitated as characteristically colored sulfides which serve to identify them.

a. Under the hood, pass hydrogen sulfide into a test tube containing zinc ions. In a similar manner prepare the sulfide precipitates of cadmium, antimony, copper and silver. Soluble tartar emetic (antimonyl potassium tartrate) is used as the source of antimony ions. Note the color of the precipitates formed. Call the pupils' attention to the Sulfide Precipitate Chart on the reference tables (page 336). Check the results of the experiment against the chart information.

Relate the activity to the use of the precipitates in making paint pigments as well as identification of unknowns.

b. In practice, the proper separation of a mixture of metallic ions requires the adjustment of *pH* and additional reactions. The more advanced chemistry student may enjoy the more complicated exercises in analysis described in college qualitative analysis manuals.

8.46. Compounds of the Alkali Metals

Compounds of the alkali metals are important because of their properties, most of which are discussed in chemistry textbooks. Possible elaborations of this high school textbook material include:

- Large deposits of these compounds are found in the earth's crust or in sea water (see reference *8R-42*).
- The solubility of the compounds makes them important reagents.
- Many of their salts undergo hydrolysis resulting in strong basic effects.
- The bonding of these salts is primarily electrovalent. Therefore, the salts of alkali metals are good electrolytes and can be electrolyzed.

8.47. Compounds of the Alkaline Earth Metals

Calcium is representative of the alkaline earth metals. *Note:* Textbooks and other sources provide a wealth of information concerning calcium compounds and exercises to illustrate their properties and uses.

The chemistry of calcium and its compounds is considered important because:

- It illustrates many principles of chemistry.
- Calcium compounds are intimately related to the natural resources of the State. The mining and processing of gypsum and limestones are important industries in New York State.
- Calcium compounds have widespread application in many fields such as agriculture, metallurgy and the building trades.

a. Calcium Carbonate

(1) Illustrate the forms of calcium carbonate by displaying as many forms of the compound as possible: limestone, marble, calcite, Iceland spar, coral, oyster and clam shells, coquina, chalk, stalagmites and stalactites, and boiler scale.

(2) Demonstrate that the forms displayed in (*1*) above may have the same chemical composition. Heat finely ground samples of the materials in an ignition tube. Pass the gas evolved into clear limewater. When the contents of the tube have become white and powdery, put the powder into a beaker containing water and a few drops of phenolphthalein. Point out that each sample has the same effect on limewater and on the phenolphthalein-water mixture. Ask the pupils to draw a conclusion. *Note:* These tests prove only that the substances are carbonates.

(3) Illustrate the property of double refraction displayed by Iceland spar. Place a sample of the Iceland spar on a ruled sheet of paper and

rotate it. Through the spar observe the lines on the paper. This property is one of the tests for Iceland spar. This demonstration may be performed with the aid of an overhead projector.

b. Calcium Oxide. Calcium oxide is also known as lime or quicklime.

(1) Demonstrate the drying action of calcium oxide. Moisten the inside of two bell jars. Place one jar over several lumps of freshly prepared quicklime. Place the other on the table as a control.

(2) Mix 1 part of Portland cement with 3 parts of fine sand. While stirring, add enough water to make a thick paste. Pour the paste into a small match box, and set it aside for a few days to harden. After several days note the appearance and hardness of the concrete.

c. Calcium Hydroxide

(1) Slake lime by adding water to freshly prepared calcium oxide. Note the large amount of heat liberated.

(2) Make some whitewash by stirring slaked lime into a beaker half full of water until a soupy suspension is formed. Use a paint brush to apply some of the whitewash to a wooden board or cardboard. After drying overnight, test the surface with a few drops of hydrochloric acid. Relate to the test for a carbonate (see activity 4.66). Account for the formation of the carbonate by the aid of equation.

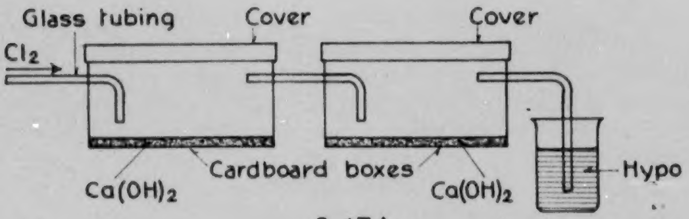
(3) Make limewater by adding 1 teaspoonful of powdered calcium hydroxide to 250 ml. of cold water. Stir. After the solution has settled, filter the suspension. Store the filtrate (limewater) in a stoppered bottle.

(4) Refer to the Table of Solubilities (see page 336) or to a chemistry handbook for the solubility of calcium hydroxide in water. Calcium hydroxide is one of the few solids more soluble in cold water than in hot water. Ask the pupils to explain why a solution of calcium hydroxide (limewater) can be saturated and, at the same time, dilute.

(5) Calcium hydroxide is used to manufacture sodium hydroxide. Add a teaspoonful of dry calcium hydroxide powder to 100 ml. of saturated sodium carbonate solution. Filter, and evaporate the filtrate to dryness. *Caution: Use the hood with the door down as far as possible; sodium hydroxide may spatter.* Relate to the soda-lime process for obtaining sodium hydroxide commercially.

d. Preparation of Bleaching Powder. *Caution: Use the hood; chlorine is poisonous.* Demonstrate the preparation of bleaching powder. Connect two cardboard boxes such as small shoe boxes in tandem as shown in diagram 8.47*d*. Place the outlet tube in a beaker of sodium thiosulfate (hypo) so that excess chlorine may be absorbed. Spread about 1/4 inch of powdered calcium hydroxide over the bottoms of the boxes. Pass chlorine gas from either a chlorine generator or a pressure tank over the calcium hydroxide.

Use the prepared bleaching powder to bleach cotton cloth, or add a drop of sulfuric acid to demonstrate the availability of chlorine.



8.47d

e. **Calcium Sulfate.** There are two hydrated forms of calcium sulfate of special interest: plaster of paris, $(CaSO_4)_2 \cdot H_2O$ and gypsum, $CaSO_4 \cdot 2H_2O$.

(1) Mix a spoonful of plaster of paris with a little water until a creamy consistency is obtained. Lubricate a glass square and a new coin with vaseline or petroleum jelly. Transfer the plaster to the glass square, and then press the coin into it. After the plaster hardens, remove the coin with a knife by prying. Slide the cast off the glass square. Note the clarity of detail and the smooth appearance of the cast.

The addition of varying amounts of acetic acid to plaster of paris pastes makes an interesting study of a *negative* catalyst.

(2) In a test tube strongly heat some crushed gypsum or the plaster made in (*1*) above. Note that water is driven off. Relate the activity to the use of gypsum in making plaster of paris.

8.48. Hard Water

a. **Testing Water for Hardness.** Test the relative hardness of natural waters. Samples may be collected from such sources as ponds, streams, rivers, cisterns, wells, springs and city supplies. To test tubes half-full of samples of the water, add two drops of soap solution (liquid soap) by means of a medicine dropper. Place the thumb over the mouth of the test tube and shake each an equal number of times. Repeat, using distilled water as a control. The amount of suds produced is a measure of the water's softness; the amount of precipitate formed is a measure of the water's hardness.

b. **Making Water Hard.** Add a small quantity of each of the following substances to each of 8 half-full test tubes of distilled water:

sodium carbonate, sugar, calcium bicarbonate, sodium chloride, calcium chloride, magnesium sulfate, iron chloride and sodium sulfate. Test each sample with 2 drops of soap solution to determine relative hardness or softness. Compare with the suds produced by using distilled water and the same amount of soap. Water containing calcium, iron and magnesium ions will prove to be hard.

c. **Preparing Water of Temporary Hardness.** Set up a carbon dioxide generator and pass the carbon dioxide into a clear limewater solution until the precipitate first formed redissolves. Filter and store for future use. Relate this activity to the natural formation of temporary hard water. Explain by the use of two equations.

d. **Preparing Water of Permanent Hardness.** Permanent hardness in natural water is caused by the presence of the sulfates of calcium, magnesium and/or iron. To prepare samples of permanently hard water in the laboratory, add a pinch (approximately ½ gm.) of any of the above sulfates to 100 ml. of water and stir. The prepared hard water may be stored indefinitely.

Test the water for hardness. Compare the results with those obtained from an equal volume of distilled water.

e. **Effect of Hard Water on Soap.** To equal volumes of water of permanent hardness, temporary hardness and distilled water in separate test tubes, add soap solution drop by drop until permanent suds form. Shake the test tube vigorously after each addition of soap solution. Keep a record of the amount of soap used. The distilled water, of course, is soft. Note the heavy precipitate formed in the samples of hard water. Emphasize how hard water wastes soap.

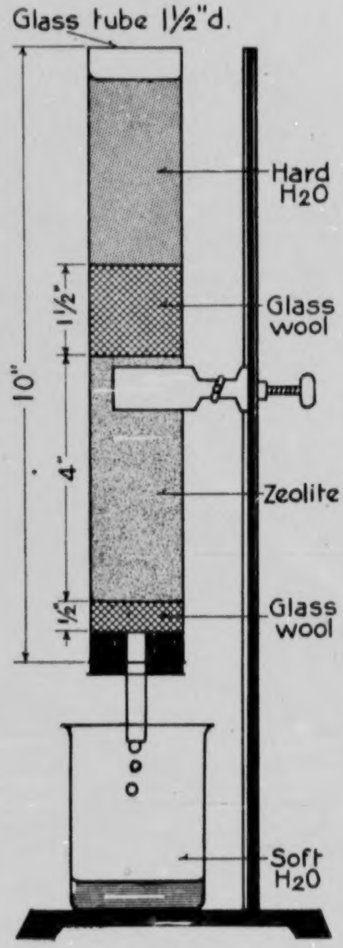
f. **Softening Water of Temporary Hardness.** Water of temporary hardness may be softened in two ways, by heating and by adding a water softener. Demonstrate each method as follows:

(1) Place a 50-ml. sample of temporarily hard water in a beaker and heat until a fine precipitate forms. Filter. Test the filtrate for softness with soap solution. Discuss the need for using soft water in steam irons.

(2) Add 1 or 2 gm. of sodium carbonate to a test tube full of temporarily hard water. Filter, and test the filtrate for softness with soap solution. In both cases, the calcium ion, the cause for water hardness, is removed from the solution. Refer to the Table of Solubilities on page 336 and compare the solubilities of the carbonates involved.

g. **Softening Water of Permanent Hardness.** Demonstrate that water of permanent hardness cannot be softened by heating. Heat 50 ml. of permanently hard water to boiling, add soap solution to show that a precipitate still forms. Add 5 gm. sodium carbonate to another 50-ml. sample of the permanently hard water, and shake. Filter, if necessary, and test filtrate for hardness. A generous quantity of soap suds will now form. Trisodium phosphate or borax (sodium tetraborate) may be substituted for the sodium carbonate as the precipitating agent.

h. Water Softening by Ionic Exchange. Show how zeolite is used to soften water by ionic exchange. Set up the apparatus as shown in diagram 8.48 *h*. Place ½ inch of glass wool in the bottom of the tube as


Glass tube 1½"d.
Hard H_2O
Glass wool
Zeolite
Glass wool
Soft H_2O
10"
1½"
4"
½"

8.48h

a retainer. Add commercial zeolite (*Permutit*) to a depth of 3 to 4 inches. Pack 1½ inch of glass wool on top of the zeolite. Fill the remainder of the glass tube to within ½ inch of the top with hard water. Collect the water and test for hardness with soap solution.

When water becomes appreciably hard again, rejuvenate the zeolite by pouring a saturated salt (NaCl) solution through the device. Rinse with distilled water, and show that the zeolite can soften water once again. The chimney zeolite water softener can be stored for use in subsequent years.

i. **Action of Soap and Detergents with Hard Water.** Demonstrate the difference in the action between soap and detergents on hard water. Water with either permanent or temporary hardness may be used with distilled water as a control.

In separate test tubes, place 50-ml. samples of permanently hard, temporarily hard and distilled water. Add 5 drops of soap solution to each to show effect of soap on the waters. Note the heavy precipitates formed.

Next test similar samples of water with different commercial detergents. Note the absence of precipitates. The calcium and magnesium salts of these substances, unlike those of soap, are soluble. Therefore detergents can emulsify grease and cleanse regardless of the hardness of the water.

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NOTES

AREA 9

Reaction Principles

9.01. Controlled Experiments and Interpretation of Data

Many of the activities related to this area are particularly suitable for controlled experiments and various forms of mathematical interpretation. For instance, in determining the effect of temperature on the velocity of a chemical change each group of pupils may obtain data for observations for different temperatures. The results may be plotted on graph paper; the results for another temperature may be predicted; the predictions may be checked by experiment.

One of the best collections of experiments in this area is found in *Scientific Experiments in Chemistry* (see bibliography). A judicious selection of these or similar experiments will lead all pupils, particularly the more able, to a better appreciation of the importance of mathematics in chemistry.

9.02. Effect of Activity of Reactants upon Velocity of Reaction

a. Place about 10 ml. of dilute hydrochloric acid in each of three test tubes. Obtain three small pieces of solid metal of approximately the same volume, such as zinc, iron and lead. Add one piece of metal to each test tube. Compare the rates at which hydrogen is evolved. Relate to the activity of the elements.

b. Place equal weights of zinc in two test tubes. To one tube add 10 ml. of concentrated hydrochloric acid, to the other add 10 ml. of dilute hydrochloric acid. Compare the rates at which the hydrogen is evolved. (See also M.C.A. Experiment No. *11*).

9.03. Effect of Temperature upon Velocity of Reaction

a. Fill two gas collecting bottles with oxygen by displacement of water. Bottled oxygen gas is convenient. Grasp a piece of steel wool with tongs and heat to red heat over a bunsen flame. Transfer the heated steel to the bottle of oxygen. Place a similar weight of unheated steel wool in the other bottle. Compare the rates of reaction.

b. A clock reaction is a spectacular and instructive demonstration. Dissolve 2 gm. of potassium iodate in one liter of water. Stopper the container; mark the container "*Solution 1.*" To 900 ml. of *cooled* water which has been freshly boiled, add 0.4 gm. of $NaHSO_3$. Also add 5 ml. of 1M sulfuric acid and 100 ml. of starch solution. Stopper the container; mark the container "*Solution 2.*"

Prepare some 1M sulfuric acid by adding 28 ml. of concentrated acid (17.8M) slowly to enough water to make 500 ml. of solution.

Prepare a starch solution by adding a small amount of water to 2 gm. of starch to make a paste. Add 100 ml. of water, heat to boiling and cool.

Add equal volumes of solutions *one* and *two* to a beaker. Note the time that elapses before a color change appears. Repeat the experiment with the reacting solutions at 25°C., at 30°C. and so on. (See M.C.A. Experiment *No. 11* for interesting variations.)

The reactions involved are:

(1) $H_2SO_4 + 2NaHSO_3 \rightarrow Na_2SO_4 + 2H_2SO_3$

(2) $H_2SO_4 + 2KIO_3 \rightarrow K_2SO_4 + 2HIO_3$

(3) $3H_2SO_3 + HIO_3 \rightarrow 3H_2SO_4 + HI$ **(oxidation of H_2SO_3)**

If any iodine appears in the solution before the H_2SO_3 has been oxidized, it is converted to HI:

$$H_2SO_3 + H_2O + I_2 \rightarrow H_2SO_4 + 2HI$$

Only after all of the H_2SO_3 has been oxidized (reason for time delay), the following rapid reaction occurs:

(4) $5HI + HIO_3 \rightarrow 3I_2 + 3H_2O$

(iodine turns blue in starch solution)

9.04. Effect of Surface Area upon Velocity of Reaction

Generally, the greater the surface area of the reactants exposed, the greater the velocity of the reaction. There are many examples of this effect, including dust explosions and reactants while in solution or colloidal suspension.

a. Heat equal weights of steel wool and iron or steel chunks over a bunsen flame and place in gas collecting bottles of oxygen. Compare the velocities of reaction.

b. Mix together gently some powdered mercuric chloride and potassium iodide. No reaction is apparent. Grind the two salts together vigorously. Note that considerable physical effort is required to produce red mercuric iodide. Prepare a second mixture of the two salts. Add water to the mixture. The same red mercuric iodide results immediately. An alternate method is to prepare separate water solutions of the two salts and mix them.

c. The choice of diluted acid to react with a solid depends upon the solubility of the product. Action of the acid takes place at the surface of the solid. If the product of the reaction is soluble in water, it is continually removed and the surface of the solid is exposed to the continued action of the acid. If, however, the reaction product is not soluble in water, it remains on the surface of the solid and in time becomes thick enough to shut off all action of the acid upon the solid.

Place equal quantities (about ½ inch) of marble chips in each of three test tubes. Add dilute sulfuric acid to one tube, dilute nitric acid to the second and dilute hydrochloric acid to the third. The action starts off briskly in all three tubes. It soon slows down and stops in the first tube since calcium sulfate is relatively insoluble. The action continues in the other tubes since calcium nitrate and calcium chloride are soluble.

Repeat the experiment using lead carbonate. The action soon stops with the hydrochloric and sulfuric acids because lead chloride and lead sulfate are relatively insoluble.

9.05. Effect of Concentration upon Velocity of Reaction

Make a solution containing approximately 10 gm. of sodium thiosulfate (hypo) in 100 ml. of solution.

Into three 150-ml. beakers, place 10.0 ml., 5.0 ml., and 2.5 ml. of solution. In the second and third beakers add 5.0 ml. and 7.5 ml. of water respectively so that each beaker contains 10 ml. of solution. Place the beakers over a sheet of lined paper on a table.

Add 10 ml. of hydrochloric acid (approximately 1N) to each beaker. View the lines on the paper by looking down through the solution. White colloidal sulfur forms in each case. With a stop watch determine the time required for the mixture to become opaque enough to make the lines invisible. Pretest the experiment and adjust the normality of the HCl if the time of reaction is not satisfactory.

This experiment may be made more quantitative by further varying the concentrations or varying the temperatures of the reactants. Graph the results using the time as the abscissa and ml. of solution as the ordinate. (See also M.C.A. Experiments *Nos. 16* and *17.*)

9.06. Effect of Pressure upon the Velocity of Reaction

Experiments in chemistry involving the effect of increased or decreased pressure are difficult to perform safely with the apparatus usually available in the chemistry laboratory. Illustrations with any pertinent industrial applications may serve to illustrate the principles involved.

In an equilibrium, if the pressure applied to the system is changed, the equilibrium point is displaced so as to reduce the effect of the change.

(1) Methyl alcohol is commercially produced, as follows:

$$\mathbf{CO\ (gas) + 2H_2\ (gas) \rightleftarrows CH_3OH\ (gas)}$$
$$\mathbf{1\ mole \qquad 2\ moles \qquad 1\ mole}$$

One mole of CO and two moles of H_2 produce one mole of CH_3OH. The CH_3OH on the right has a smaller volume. An increase in pressure brings about the production of more CH_3OH which reduces the pressure. Similar effects are noted in the Haber process. Compare the yield of ammonia at different pressures from data available in many textbooks.

(2) In another industrial process toluene is manufactured by the dehydrogenation of methylcyclohexane, as follows:

$$\mathbf{C_7H_{14}\ (gas) \rightleftarrows C_7H_8\ (gas) + 3H_2\ (gas)}$$
$$\mathbf{1\ mole \qquad 1\ mole \qquad 3\ moles}$$

In this case, as the reaction proceeds to the right there is an increase in the number of molecules. An increase in pressure causes the equilibrium to shift to the *left*. In order to produce more toluene, pressure is reduced and the equilibrium point moves to the right.

(3) Carbon dioxide is reduced by hydrogen, as follows:

$$\mathbf{CO_2\ (gas) + H_2\ (gas) \rightleftarrows CO\ (gas) + H_2O\ (gas)}$$
$$\mathbf{1\ mole \qquad 1\ mole \qquad 1\ mole \qquad 1\ mole}$$

In this case, there are two moles on either side of the equation. A change in pressure will *not* shift the equilibrium point.

9.07. Effect of a Catalyst upon the Velocity of Reaction

Prepare oxygen by the same general method described in activity 4.12*d* using a peroxide with potassium permanganate or manganese dioxide. Place equal volumes of the peroxide in test tubes. Add varying known weights of the catalyst to the peroxide. Measure the volume of oxygen collected in identical bottles in a given time. Plot the results using weight of catalyst as the abscissa and volume of oxygen collected on the ordinate. (See also M.C.A. Experiment *No. 20*.)

9.08. Chemical Equilibrium

The quantitative aspects of chemical equilibrium not only are challenging to the more able students, but also provide them with considerable practice in handling the slide rule and using powers of ten (see appendix *E-2*). Many illustrations are available in college level textbooks.

a. General Equation of Equilibrium. Any reversible chemical reaction may be represented by the general equation:

$$\mathbf{aA + bB \rightleftarrows cC + dD}$$

where the small letters represent the coefficients in the equation, *A* and *B* represent the *reactants*, and *C* and *D* represent the *products*. The general equation may be applied to specific equations, as follows:

(1) $\mathbf{aA + bB \rightleftarrows cC + dD}$
$\mathbf{1\ CH_3OH + 1\ HCOOH \rightleftarrows 1\ HCOOCH_3 + 1\ H_2O}$
where a = b = c = d = 1 and A = CH_3OH, B = HCOOH, C = $HCOOCH_3$, D = H_2O.

(2) $\mathbf{aA + bB \rightleftarrows cC}$
$\mathbf{1\ H_2 + 1\ Br_2 \rightleftarrows 2\ HBr}$.
Note that *dD* is missing since there is only one product.

(3) $\mathbf{aA \rightleftarrows cC + dD}$
$\mathbf{1\ NH_4OH \rightleftarrows 1\ NH_4^+ + 1\ OH^-}$
Note that the *bB* is missing since there is only one reactant.

b. Law of Mass Action. The reactions in a dilute aqueous solution of acetic acid may be represented by the equation:

$$\mathbf{HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-}$$

The Law of Mass Action states that the rate of reaction is directly proportional to the concentration of each of the reacting substances. Initially the reaction is to the right. As the reaction to the right continues, the concentration of the products increases, and, according to the Law of Mass Action, the rate at which H^+ ions and $C_2H_3O_2^-$ ions recombine to form molecular $HC_2H_3O_2$ increases. Equilibrium is reached when the rates of reaction in both directions are equal. At equilibrium the concentrations of the various substances can be related to each other in the following manner:

$$K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b} \text{ where } K_c = \text{equilibrium constant}$$

[ ] = concentration in moles per liter.

K_c, the equilibrium constant, is a numerical value that varies very little for any given chemical reaction at a particular temperature, even though the concentrations of the substances involved may increase or decrease.

c. Determination of the Equilibrium Constant. The value of the equilibrium constant for a reaction at a specific temperature may be determined by precise analysis using equipment not normally available in the high school laboratory. To illustrate the determination of K_c for a dilute aqueous solution of pure acetic acid at 25°C., the following data were obtained:

	START	AT EQUILIBRIUM (25°C.)		
	$HC_2H_3O_2$ MOLES/LITER	H^+ MOLES/LITER	$C_2H_3O_2^-$ MOLES/LITER	$HC_2H_3O_2$ MOLES/LITER
Case 1	0.0102	0.00042	0.00042	0.0098
Case 2	0.0039	0.00026	0.00026	0.0037
Case 3	0.0017	0.00017	0.00017	0.0016

The equilibrium reaction is represented as:

$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-$$

The equation, $K_e = \dfrac{[C]^c \times [D]^d}{[A]^a}$

$$K_e = \frac{[H^+]^1 \times [C_2H_3O_2^{-1}]^1}{[HC_2H_3O_2]^1}$$

Case 1: $K_e = \dfrac{(.00042)^1 \times (.00042)^1}{(.0098)^1} = \dfrac{(4.2 \times 10^{-4})^1 (4.2 \times 10^{-4})^1}{(9.8 \times 10^{-3})^1}$
$= 1.8 \times 10^{-5}$

Case 2: $K_e = \dfrac{(.00026)^1 \times (.00026)^1}{(.0037)^1} = \dfrac{(2.6 \times 10^{-4})^1 (2.6 \times 10^{-4})^1}{(3.7 \times 10^{-3})^1}$
$= 1.8 \times 10^{-5}$

Case 3: $K_e = \dfrac{(.00017)^1 \times (.00017)^1}{(.0016)^1} = \dfrac{(1.7 \times 10^{-4})^1 (1.7 \times 10^{-4})^1}{(1.6 \times 10^{-3})^1}$
$= 1.8 \times 10^{-5}$

Note: Generally, only exponents other than "1" are indicated.

See appendix *E-2* for rules relating to powers of ten.

The equilibrium constant K_e is apparently the same for the three dilute aqueous solutions of pure acetic acid at 25°C. However, if the results were determined using three significant figures rather than two, a slight variation in the value of K_e would be noted.

9.09. Shifting the Equilibrium Point

The effect of a change of concentration on the equilibrium point may be vividly demonstrated.

a. Dissolve a small amount of antimony (III) chloride in hydrochloric acid. Add water and note the white precipitate, $Sb(OH)Cl_2$.

Slowly add concentrated HCl. Note the disappearance of the precipitate as the reaction reverses. Add additional water and note the change.

$$SbCl_3 + H_2O \rightleftharpoons Sb(OH)Cl_2 + HCl$$

b. To 100 ml. of water in a 500-ml. beaker, add bismuth (III) chloride, with constant stirring, until a noticeable amount of precipitate (BiOCl) forms. The equation for the equilibrium mixture resulting from the partial hydrolysis of the salt follows:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$

The addition of water to the equilibrium mixture will cause the reaction to go to the right resulting in the formation of more precipitate. Add some dilute HCl. Observe that the action is reversed and that the precipitate disappears.

9.10. Catalysts Bring About Chemical Reactions

To illustrate a reduction-oxidation (redox) reaction, add approximately 4 gm. of glucose, 4 gm. of potassium hydroxide and 2 or 3 drops of methylene blue to 175 ml. of water in a 250-ml. flask, and stopper. (Amounts used are not critical.)

Initially the color of the solution will be blue because an activated complex is formed between the methylene blue and the oxygen dissolved in the water. The oxygen in the complex is reduced by the glucose which, in turn, is oxidized. When the oxygen is removed from the complex, the solution becomes colorless.

Shake the flask. Oxygen from the air in the flask mixes with the solution and a blue color again results. On standing, the solution again becomes colorless. Repeating this procedure will result in the same color changes until the oxygen in the flask has been depleted. If the stopper is removed for a short time and then replaced, the color changes can again be produced.

In this illustration the methylene blue acts as a catalyst to the reaction between glucose and oxygen. This effect is somewhat analagous to that of oxygen being taken up by the hemoglobin of the blood until the oxygen is reduced by food in the body.

NOTES

THE UNIVERSITY OF THE STATE OF NEW YORK
THE STATE EDUCATION DEPARTMENT
BUREAU OF SECONDARY CURRICULUM DEVELOPMENT
ALBANY

Reference Tables for Chemistry

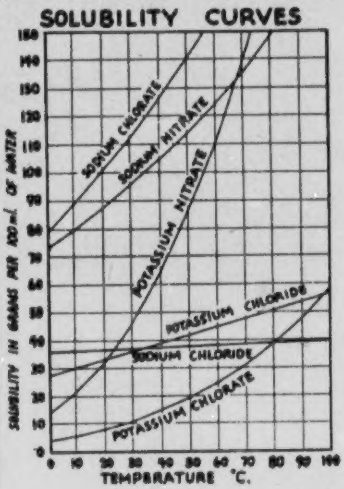
RELATIVE DEGREE OF IONIZATION OF SOME ACIDS AND BASES

ACIDS			BASES	
completely or nearly completely ionized	moderately ionized	slightly ionized	completely or nearly completely ionized	slightly ionized
nitric	oxalic	hydrofluoric	potassium hydroxide	ammonium hydroxide
hydrochloric	phosphoric	acetic	sodium hydroxide	(all others)
sulfuric	sulfurous	carbonic	barium hydroxide	
hydriodic		hydrosulfuric	strontium hydroxide	
hydrobromic		(all others)	calcium hydroxide	

DENSITY AND SOLUBILITY OF SOME COMMON GASES

NAME	DENSITY gram/liter 0°C. 760 mm.	SOLUBILITY in cold water 760 mm.
air	1.29	SS
ammonia	0.77	ES
carbon dioxide	1.98	MS
carbon monoxide	1.25	SS
chlorine	3.21	MS
helium	0.18	SS
hydrogen	0.09	SS
hydrogen chloride	1.64	ES
hydrogen sulfide	1.54	MS
nitrogen	1.25	SS
oxygen	1.43	SS
sulfur dioxide	2.93	VS

SS = SLIGHTLY SOLUBLE   MS = MODERATELY SOLUBLE
VS = VERY SOLUBLE   ES = EXTREMELY SOLUBLE



PERIODIC TABLE

ATOMIC WEIGHTS ARE GIVEN TO FOUR SIGNIFICANT FIGURES IN MOST CASES. WHEN USED IN SOLVING PROBLEMS, THESE WEIGHTS MAY BE ROUNDED OFF TO THE NEAREST WHOLE NUMBER. 1952 INTERNATIONAL ATOMIC WEIGHTS ARE USED.

ATOMIC WEIGHTS IN BRACKETS DENOTE THE MOST STABLE KNOWN ISOTOPE.

GROUPS

PERIOD	IA	IIA	III B	IVB	VB	VIB	VIIB	VIII	VIII	VIII
1	$_{1}\mathrm{H}^{1.008}$ 1									
2	$_{3}\mathrm{Li}^{6.940}$ 2-1	$_{4}\mathrm{Be}^{9.013}$ 2-2								
3	$_{11}\mathrm{Na}^{22.99}$ 2-8-1	$_{12}\mathrm{Mg}^{24.32}$ 2-8-2								
4	$_{19}\mathrm{K}^{39.10}$ 2-8-8-1	$_{20}\mathrm{Ca}^{40.08}$ 2-8-8-2	$_{21}\mathrm{Sc}^{44.96}$ 2-8-9-2	$_{22}\mathrm{Ti}^{47.90}$ 2-8-10-2	$_{23}\mathrm{V}^{50.95}$ 2-8-11-2	$_{24}\mathrm{Cr}^{52.01}$ 2-8-13-1	$_{25}\mathrm{Mn}^{54.94}$ 2-8-13-2	$_{26}\mathrm{Fe}^{55.85}$ 2-8-14-2	$_{27}\mathrm{Co}^{58.94}$ 2-8-15-2	$_{28}\mathrm{Ni}^{58.71}$ 2-8-16-2
5	$_{37}\mathrm{Rb}^{85.48}$ 2-8-18-8-1	$_{38}\mathrm{Sr}^{87.63}$ 2-8-18-8-2	$_{39}\mathrm{Y}^{88.92}$ 2-8-18-9-2	$_{40}\mathrm{Zr}^{91.22}$ 2-8-18-10-2	$_{41}\mathrm{Nb}^{92.91}$ 2-8-18-12-1	$_{42}\mathrm{Mo}^{95.95}$ 2-8-18-13-1	$_{43}\mathrm{Tc}^{(99)}$ 2-8-18-14-1	$_{44}\mathrm{Ru}^{101.1}$ 2-8-18-15-1	$_{45}\mathrm{Rh}^{102.9}$ 2-8-18-16-1	$_{46}\mathrm{Pd}^{106.7}$ 2-8-18-18
6	$_{55}\mathrm{Cs}^{132.9}$ 2-8-18-18-8-1	$_{56}\mathrm{Ba}^{137.4}$ 2-8-18-18-8-2	$_{57}\mathrm{La}^{138.9}$ 2-8-18-18-9-2	$_{72}\mathrm{Hf}^{178.6}$ -18-32-10-2	$_{73}\mathrm{Ta}^{180.9}$ -18-32-11-2	$_{74}\mathrm{W}^{183.9}$ -18-32-12-2	$_{75}\mathrm{Re}^{186.2}$ -18-32-13-2	$_{76}\mathrm{Os}^{190.2}$ -18-32-14-2	$_{77}\mathrm{Ir}^{192.2}$ -18-32-15-2	$_{78}\mathrm{Pt}^{195.1}$ -18-32-17-1
7	$_{87}\mathrm{Fr}^{(223)}$ -18-32-18-8-1	$_{88}\mathrm{Ra}^{226}$ -18-32-18-8-2	$_{89}\mathrm{Ac}^{227}$ -18-32-18-9-2							

NOTE: The electronic structures of elements Nos 72-89 are shown incomplete. These elements have 2 electrons in the first ring and 8 in the second.

LANTHANIDE SERIES

Ce^{140} 58	Pr^{141} 59	Nd^{144} 60	$\mathrm{Pm}^{(145)}$ 61	Sm^{150} 62	Eu^{152} 63	Gd^{157} 64	Tb^{159} 65	Dy^{163} 66	Ho^{165} 67	Er^{167} 68	Tm^{169} 69	Yb^{173} 70	Lu^{175} 71

ACTINIDE SERIES

Th^{232} 90	Pa^{231} 91	U^{238} 92	$\mathrm{Np}^{(237)}$ 93	$\mathrm{Pu}^{(242)}$ 94	$\mathrm{Am}^{(243)}$ 95	$\mathrm{Cm}^{(245)}$ 96	$\mathrm{Bk}^{(249)}$ 97	Cf [illegible] 98	$\mathrm{Es}^{(254)}$ 99	Fm [illegible] 100	Md [illegible] 101	No [illegible] 102	103

HALF-LIVES OF SOME RADIOISOTOPES

$_{6}\mathrm{C}^{14}$	5,580 yrs.
$_{27}\mathrm{Co}^{60}$	5.3 yrs.
$_{79}\mathrm{Au}^{198}$	2.7 days

$_{53}\mathrm{I}^{131}$	8 days
$_{15}\mathrm{P}^{32}$	14.3 days
$_{38}\mathrm{Sr}^{90}$	20 yrs.

SYMBOLS OF SOME PARTICLES

electron	$_{-1}\mathrm{e}^{0}$
proton	$_{1}\mathrm{H}^{1}$
neutron	$_{0}\mathrm{n}^{1}$

alpha particle	$_{2}\mathrm{He}^{4}$
deuteron	$_{1}\mathrm{H}^{2}$
triton	$_{1}\mathrm{H}^{3}$

OF THE ELEMENTS

KEY

ATOMIC WEIGHT
SYMBOL
ATOMIC NUMBER
ELECTRONIC STRUCTURE

GROUPS

I B	II B	III A	IV A	V A	VI A	VII A	O
							$_{2}\mathrm{He}^{4.003}$ 2
		$_{5}\mathrm{B}^{10.82}$ 2-3	$_{6}\mathrm{C}^{12.01}$ 2-4	$_{7}\mathrm{N}^{14.01}$ 2-5	$_{8}\mathrm{O}^{16.00}$ 2-6	$_{9}\mathrm{F}^{19.00}$ 2-7	$_{10}\mathrm{Ne}^{20.18}$ 2-8
		$_{13}\mathrm{Al}^{26.98}$ 2-8-3	$_{14}\mathrm{Si}^{28.09}$ 2-8-4	$_{15}\mathrm{P}^{30.98}$ 2-8-5	$_{16}\mathrm{S}^{32.07}$ 2-8-6	$_{17}\mathrm{Cl}^{35.46}$ 2-8-7	$_{18}\mathrm{Ar}^{39.94}$ 2-8-8
$_{29}\mathrm{Cu}^{63.54}$ 2-8-18-1	$_{30}\mathrm{Zn}^{65.38}$ 2-8-18-2	$_{31}\mathrm{Ga}^{69.72}$ 2-8-18-3	$_{32}\mathrm{Ge}^{72.60}$ 2-8-18-4	$_{33}\mathrm{As}^{74.91}$ 2-8-18-5	$_{34}\mathrm{Se}^{78.96}$ 2-8-18-6	$_{35}\mathrm{Br}^{79.92}$ 2-8-18-7	$_{36}\mathrm{Kr}^{83.80}$ 2-8-18-8
$_{47}\mathrm{Ag}^{107.9}$ 2-8-18-18-1	$_{48}\mathrm{Cd}^{112.4}$ 2-8-18-18-2	$_{49}\mathrm{In}^{114.8}$ 2-8-18-18-3	$_{50}\mathrm{Sn}^{118.7}$ 2-8-18-18-4	$_{51}\mathrm{Sb}^{121.8}$ 2-8-18-18-5	$_{52}\mathrm{Te}^{127.6}$ 2-8-18-18-6	$_{53}\mathrm{I}^{126.9}$ 2-8-18-18-7	$_{54}\mathrm{Xe}^{131.3}$ 2-8-18-18-8
$_{79}\mathrm{Au}^{197.}$ -18-32-18-1	$_{80}\mathrm{Hg}^{200.6}$ -18-32-18-2	$_{81}\mathrm{Tl}^{204.4}$ -18-32-18-3	$_{82}\mathrm{Pb}^{207.2}$ -18-32-18-4	$_{83}\mathrm{Bi}^{209.0}$ -18-32-18-5	$_{84}\mathrm{Po}^{210}$ -18-32-18-6	$_{85}\mathrm{At}^{(211)}$ -18-32-18-7	$_{86}\mathrm{Rn}^{222}$ -18-32-18-8

NATURAL ISOTOPES OF SOME COMMON ELEMENTS

$_{1}H^{1}$	$_{1}H^{2}$
$_{2}He^{4}$	$_{2}He^{3}$
$_{3}Li^{7}$	$_{3}Li^{6}$
$_{5}B^{11}$	$_{5}B^{10}$
$_{6}C^{12}$	$_{6}C^{13}$
$_{7}N^{14}$	$_{7}N^{15}$

$_{8}O^{16}$	$_{8}O^{18}$	$_{8}O^{17}$
$_{10}Ne^{20}$	$_{10}Ne^{22}$	$_{10}Ne^{21}$
$_{12}Mg^{24}$	$_{12}Mg^{26}$	$_{12}Mg^{25}$
$_{14}Si^{28}$	$_{14}Si^{29}$	$_{14}Si^{30}$
$_{17}Cl^{35}$	$_{17}Cl^{37}$	
$_{92}U^{238}$	$_{92}U^{235}$	$_{92}U^{234}$

SOME COMMON VALENCES NOT READILY FOUND BY USING PERIODIC TABLE

NH_4^+	Pb^{++}	NO_2^-
Hg_2^{++}	CH_3COO^-	NO_3^-
Cu^{++}	ClO_3^-	CO_3^{--}
Sn^{++}	HCO_3^-	SO_3^{--}
Sb^{+++}	HSO_3^-	SO_4^{--}
Cr^{+++}	HSO_4^-	PO_4^{---}
Fe^{+++}	OH^-	

ELECTROMOTIVE SERIES

METALS

K
Ca
Na
Mg
Al
Zn
Cr
Fe
Ni
Sn
Pb
H
Cu
Hg
Ag
Pt
Au

HALOGENS

F
Cl
Br
I

pH VALUES for EQUIVALENT (0.1N) SOLUTIONS

hydrochloric acid	1.1	alum	3.2	ammonium hydroxide	11.1
sulfuric acid	1.2	boric acid	5.2	sodium carbonate	11.6
phosphoric acid	1.5	pure water	7.0	trisodium phosphate	12.0
citric acid	2.2	sodium bicarbonate	8.4	sodium hydroxide	13.0
acetic acid	2.9	borax	9.2	potassium hydroxide	13.0

FLAME TESTS

Na	yellow	Ca	orange-red
K	violet	Ba	yellow-green
Li	crimson	Cu	blue-green
Sr	red-scarlet		

SULFIDE PRECIPITATES

Sb	orange	Cu	black
As	yellow	Pb	black
Bi	brown	Ag	black
Cd	yellow	Zn	white

TABLE OF SOLUBILITIES IN WATER

i – nearly insoluble Ss – slightly soluble s – soluble d – decomposes	ACETATE	BROMIDE	CARBONATE	CHLORIDE	HYDROXIDE	IODIDE	NITRATE	OXIDE	PHOSPHATE	SULFATE	SULFIDE
aluminum	s	s		s	i	s	s	i	i	s	d
ammonium	s	s	s	s	s	s	s		s	s	s
barium	s	s	i	s	s	s	s	s	i	i	d
calcium	s	s	i	s	Ss	s	s	Ss	i	Ss	d
copper II	s	s	i	s	i		s	i	i	s	i
iron II	s	s	i	s	i	s	s	i	i	s	i
iron III	s	s		s	i	s	s	i	i	Ss	d
lead	s	Ss	i	Ss	i	Ss	s	i	i	i	i
magnesium	s	s	i	s	i	s	s	i	i	s	d
mercury I	Ss	i	i	i		i	s	i	i	Ss	i
mercury II	s	Ss	i	s	i	i	s	i	i	d	i
potassium	s	s	s	s	s	s	s	s	s	s	s
silver	Ss	i	i	i		i	s	i	i	Ss	i
sodium	s	s	s	s	s	s	s	d	s	s	s
zinc	s	s	i	s	i	s	s	i	i	s	i

Appendix A

Working in the Chemistry Laboratory

A-1. Safety in the Chemistry Laboratory

All activities in this handbook *must* be conducted under carefully controlled conditions. The teacher is responsible for taking every precaution to safeguard the pupils. Most accidents *can* be prevented if the teacher and pupils place the proper emphasis upon safety. A knowledge of the hazards which exist in the chemistry laboratory and the development of proper laboratory techniques are the two most vital steps in safety education.

The Safety Record of Industry

To millions the word "chemical" is still synonymous with "explosion" or "poison." The stock query to chemistry pupils is "What did you blow up today?" True, the fact that some chemicals are poisonous or explosive and potentially dangerous unless properly handled is perhaps the reason the chemical industry has such a splendid record. From necessity it has been safety-conscious. The chemical industry averages 3.38 injuries for every million man-hours, compared with 6.38 for all industry. Man-hours lost are 37 percent below the national industrial average. It is one of the 10 safest industries. Because of incessant vigilance and training in *proper methods* of handling chemicals, one of the safest places a person can be is in a modern chemical plant or nuclear research laboratory.

Safety Is an Attitude

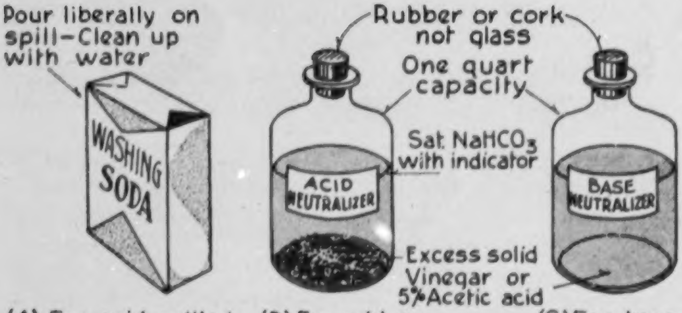
Safety in the high school chemistry course needs to be much more than merely a few "safety tips" on handling acids. Attitude is what makes a pupil safe. The development of a proper attitude toward safety while young will multiply advantages in all activities throughout life. Teachers are obliged to realize how readily pupils perceive and imitate the attitudes they find in grown-ups they admire. The following attitudes and realizations are important considerations for both teacher and pupil:

- Safety is an important subject.
- Safety is an integral part of the study of chemistry.
- The chemical industry has a marvelous safety record; the high school laboratory must have.
- An attitude of "it can't happen to me" creeps up on all of us. We must realize this, and strive to have a habit of self-criticism and a desire to maintain a positive, militant safety-consciousness.

General Safety Suggestions

The teacher of chemistry is urged to consider carefully the following recommendations to provide for the safety of his pupils:

- Devote several sessions a year to the topic of safety. Since the impression you create wears off rapidly, these sessions should be spread out, rather than occurring all in one part of the course.
- Equip the laboratory with sensible safety devices such as a first aid cabinet, CO_2 fire extinguisher, fire blankets, safety goggles and emergency charts. Describe their use to the pupils, and set the example by using them yourself in appropriate situations.
- Keep a reference, such as the *Handbook of Dangerous Materials* by Sax, on hand in the laboratory.
- Give special attention to the storage of flammables and other dangerous materials. The manufacturers will in most cases provide necessary details. There may be specific school and municipal regualtions in this regard.
- Post a list of laboratory regulations and make the pupils responsible to know and to follow them.
- Prepare a bulletin display on safety. (The du Pont booklet, *The Story of Safety*, is very useful here.) Include charts such as the one shown in diagram *A-1a*.
- Require written reports on all accidents, even small ones. A printed form will add seriousness to this regulation.
- All chemicals are safe when handled with proper precautions. New chemicals are regarded as unsafe until thoroughly tested under all conditions.
- To the beginner, all chemicals are "new."
- Almost all chemicals, however innocent in name, appearance or previous uses, can be made dangerous by placing them in the hands of an inexperienced person.
- Knowledge of potential hazards is the chemist's principal shield against injury. *When he doesn't know, he looks it up.* He knows where to look.


Pour liberally on spill—Clean up with water
WASHING SODA
Rubber or cork not glass
One quart capacity
Sat. $NaHCO_3$ with indicator
ACID NEUTRALIZER
BASE NEUTRALIZER
Excess solid
Vinegar or 5% Acetic acid

(A) For acid spilled on desk or floor (B) For acid on hands or clothes (C) For base on hands or clothes

A-1a

- **Most professional chemists *never* experiment with explosives. It is a highly specialized branch of work, requiring years of training.**
- **Rocket fuels are "controlled" explosives. High school teachers and pupils cannot be regarded as qualified to experiment safely with such fuels, or any similar combination of fuel and oxidizer.**
- **Micro and semimicro experiments and demonstrations are inherently safer than conventional ones.**
- **When a group is present, no one is safer than the least safe person. Safety is a cooperative project. Experienced laboratory workers refuse to work near a careless person.**
- **Every person working in a laboratory should undergo a period of instruction in safety for that particular laboratory. During this training he should actually operate all the safety devices. New teachers in a school should be carefully instructed by an experienced person in regard to safety equipment and regulations.**
- **Many demonstrations and experiments have been omitted from this handbook because of the possibility of considerable danger to the teacher and/or pupils. Some demonstrations included have been designated *TEACHER DEMONSTRATION ONLY* and are accompanied by warnings of specific dangers. All demonstrations should be performed by the teacher if they are new and untested, or when the chemicals or equipment are not exactly as recommended in the directions, or if special dangers are noted.**

A-2. First Aid Treatment in the Chemistry Laboratory

Policy

Teachers should be familiar with first aid treatment and be able to administer it satisfactorily. If a pupil under a teacher's jurisdiction is injured, the teacher is required to administer first aid. The school physician or nurse, when immediately present, should take care of any serious emergency. In their absence, any member of the school personnel should administer first aid, and the school administrator or his representative should contact the parents immediately.

Treatment of a pupil by any of the school personnel is limited to first aid treatment only. Any further treatment is the responsibility of the parent or legal guardian.

Making a "Universal" Antidote

Normally, nothing should be given internally except in an emergency. In the case when a pupil is suspected of having taken an unknown kind of poison internally, a "universal" antidote is sometimes used.

The "universal" antidote is made by mixing thoroughly one part by weight of magnesium oxide, one part of tannic acid and two parts of powdered charcoal. Place the mixture in a clean, dry box or bottle. A label should be attached, giving the name, use and dosage (one heaping teaspoonful in a small glass of warm water). Store in first aid chest or wherever other first aid supplies are kept in the laboratory.

Emergency Kits

An emergency kit should be provided for the use of a physician, nurse-teacher, classroom teacher or other responsible person, in case of an accident or emergency where it is impossible to bring the injured or ill person to the health room. This kit may be a strong cloth bag or a box plainly marked *Emergency Kit* and should contain:

- Triangular bandages
- Gauze bandages (1-inch and 2-inch)
- Gauze dressings (sterile, various sizes)
- Absorbent cotton
- Adhesive
- Applicators (cotton tipped)
- Tongue depressors
- A small bottle of a standard selected antiseptic
- Scissors
- A tube of petrolatum
- A small package of sodium bicarbonate marked "bicarbonate of soda for burns"

Helpful Safety Aids

The Fisher Scientific Company distributes free to schools two excellent publications dealing with the topic of safety.

(1) *Laboratory Emergency Chart*

This chart makes an excellent ready reference for first aid for the chemistry laboratory and should be posted in a conspicuous place. It includes recommended first aid treatment for the following:

- Burns and scalds
- Cuts
- Collapse
- Toxic headaches
- Electrical shock
- Emergency treatment for poisoning (including treatments for specific poisoning)
- Artificial respiration

(2) *Manual of Laboratory Safety*

This pamphlet contains specific suggestions dealing with:

- Accident prevention
- First aid
- Fire prevention
- Safety equipment

These publications may be received free by writing to Fisher Scientific Company, 633 Greenwich Street, New York 14.

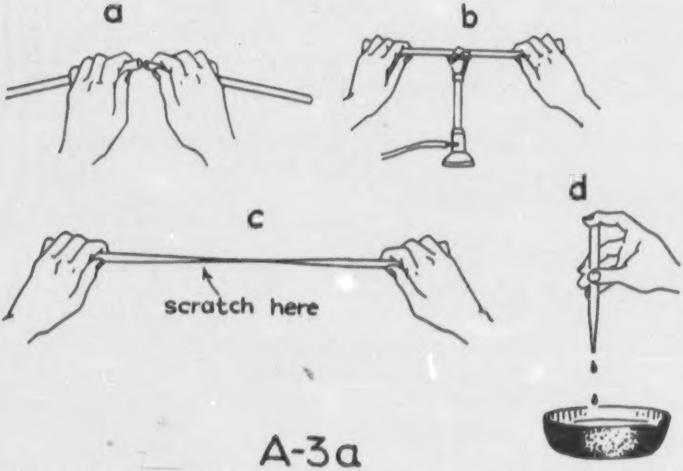
A-3. Technical Procedures

Making and Using a Pipette

Pupils can easily make a pipette for transferring small amounts of liquid from one vessel to another. Place a 2-foot length of glass tubing on a flat surface and make a deep scratch across it with a triangular file. Hold the tubing so that the cut is away from the body and grasp the glass so that the thumbs are behind the scratch. Using the thumbs as a fulcrum, gently pull the glass tubing toward the body. The glass should break easily at the scratch mark.

The ends of glass tubing should always be fire-polished. Hold the tubing so that one end is just above the blue cone of a bunsen flame. Rotate the glass and remove it as soon as the end appears to be smooth. Caution pupils about touching hot glass since serious burns may occur. The polished end should be completely cooled before fire-polishing the other end.

Heat the center of a 12-inch length of tubing and keep rotating the glass in the flame until it becomes pliable and soft. Remove the tubing



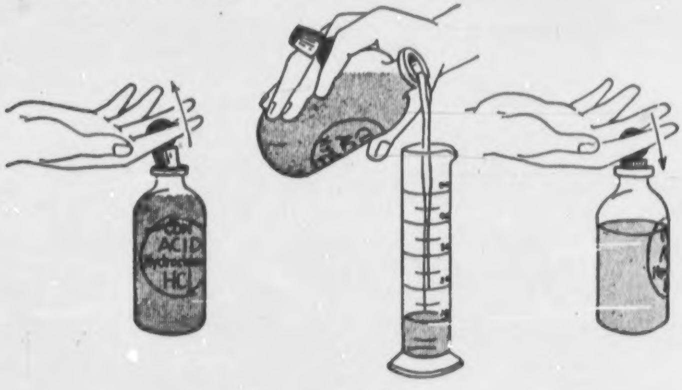
A-3a

from the burner and slowly pull the ends in opposite directions. The heated area will stretch into a fine capillary tube. Cut at the thin center to form two pipettes.

When the two pipettes have cooled, lower one of them into a test tube of water. When the water has risen in the tube, place the index finger firmly over the top of the pipette. Then remove the finger. See diagram *A-3a*.

Pouring Liquids

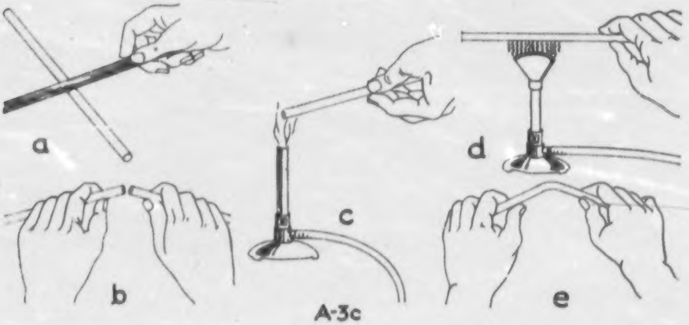
Diagram *A-3b* illustrates the proper procedure to use when pouring liquids from a bottle.



A-3b

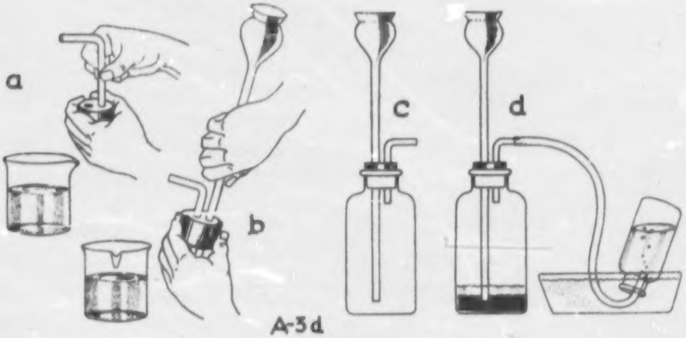
Assembling Apparatus for Making and Collecting Gases

Fire polish the ends of an 8-inch length of glass tubing. Now with a wing top in the burner hold the tubing lengthwise above the flame of a burner with a wing top as shown in diagram *A-3c*. Rotate the tubing with both hands, and heat the center section until it becomes soft and pliable. Remove the glass from the flame and bend it to form a right angle. If the hot glass is placed on an asbestos square, the corner of the square can be used as a guide for making the right angle.



A-3c

The teacher should demonstrate the correct method for inserting a glass bend and thistle tube into a stopper. Point out that the glass must be wet before the tube is twisted into the stopper. Point out also that the tube should be held near the stopper while twisting and pushing it rather than at the bend or by the thistle. Explain to pupils why the end of the thistle tube must be under the surface of the liquid in a gas generator and how the thistle tube acts as a safety device. See diagram *A-3d*.



A-3d

To collect gases that are not readily soluble in water, fill a pneumatic trough or other overflow pan with water. Fill two or three collecting bottles with water and cover them with glass plates. Holding the covers on tightly, invert the bottles, set them in the pan and remove the plate. Put the end of the delivery tube in the mouth of one of the bottles. If the pan has a shelf with a hole in it, set the bottle over the hole first and then introduce the delivery tube into it. When the bottle is filled with gas, cover it again with the glass plate and remove it from the water. Fill the remaining bottles the same way.

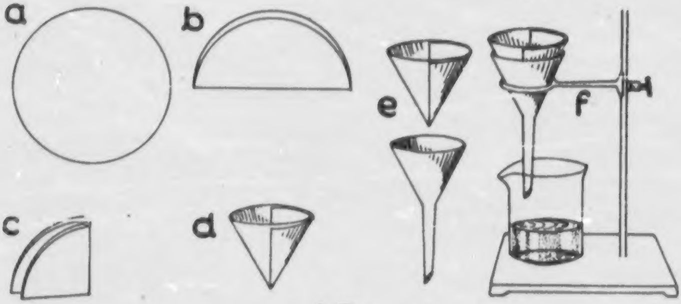
If a gas collected is heavier than air, set the filled bottles upright. If the gas is lighter than air, set the bottles on the glass plates in the inverted position.

When dismantling the generator, leave the thistle tube in the rubber stopper for future use.

To collect gases that are readily soluble in water requires that the gases be collected in some manner other than the general method illustrated in diagram *A-3d*. Generally, gases lighter than air are collected by the downward displacement of air, and gases heavier than air are collected by the upper displacement of air. Laboratory manuals for high school chemistry contain diagrams and specific instructions for the preparation and collection of gases such as ammonia, which is lighter than air, and chlorine, which is heavier than air.

Filtering Liquids

The proper steps involved in the filtering of liquids are illustrated in diagram *A-3e*.



A-3e

Using the Balance

The ordinary platform balance is satisfactory for most purposes in a beginning chemistry course. Usually, this type of balance is accurate to 0.1 gm. To carry out more precise work a balance of greater sensitivity will be required and usually the techniques of weighing are more involved. Specific instructions accompany each type of balance. The teacher and pupils should not attempt to use the various types of balances until they are familiar with the proper procedures which include:

- Before using a balance be sure that the weighing pan or pans are clean and that the pointer oscillates freely over the range of the attached scale when the "slider" is set at zero.
- Determine the "rest point" of the balance. The correct procedure is usually included in the instructions that accompanied the balance. Many laboratory manuals contain instructions for determining the rest point.
- If weighing paper is to be used, place the square(s) on the platform(s) before determining the rest point.
- Weighing paper usually consists of squares of glazed paper. Discs of filter paper may be used if glazed paper is not available.
- When using a platform balance, always put the object to be weighed on the left platform (when facing the front of the balance) and the weights on the right platform.
- Add larger weights first and continue to add weights until the additional weight required can be added by moving the slide along the scale on the balance.
- The use of larger weights first reduces the number of weights required which in turn reduces the chance for error and the time required for weighing. It also makes the smaller weights available when they are needed.
- Don't drop objects to be weighed or weights carelessly on the balance. Jarring the balance unnecessarily may result in damage to the bearing surfaces and a consequent loss of sensitivity of the balance.
- Keep the weights clean and avoid damage to them by dropping and exposure to corrosion.
- After using balance, return the weights to their container, making sure none has been misplaced.

Using the Hood

To eliminate poisoning by gases or fumes in the laboratory or classroom, care must be taken to avoid inhaling them even in low concentrations for a short time. The sense of smell is not a reliable guide to detect poisonous gases. Some of the most dangerous gases have a pleasant odor or none at all.

Properly installed hoods should have:

- The exhaust terminated in a safe place to prevent contaminants returning into the building
- Separate ventilation, each having its own exhaust fan and duct
- Exhaust fans that are spark-proof and corrosion-resistant
- Doors with full-vision panes of safety glass
- Doors that are counterbalanced so that they can be raised or lowered easily and that stop 1 inch from the bottom to permit adequate ventilation

The hood should be in good working order and the importance of using it impressed upon the pupils by the good example set by the teacher by:

- Using the hood when working with gases such as carbon monoxide, hydrogen sulfide, chlorine, sulfur dioxide and nitrogen dioxide
- Using the hood when working with liquids such as benzene, ether, carbon disulfide, methyl alcohol and carbon tetrachloride
- Not using the hood as a storage place for textbooks, laboratory manuals and science apparatus

Using the Bunsen Burner

The bunsen burner is used to mix air and gas in order to obtain a desired type of flame. A clear blue flame that burns with a minimum of noise is best for most purposes. Skill at varying the air and gas mixture to produce the desired type of flame should be acquired. Specific details regarding the use of the bunsen burner can be found in most high school laboratory manuals. *CAUTION: Keep face and other parts of the body to one side of the bunsen burner when lighting the gas.*

- To light burner turn the gas on partially (keep air supply to a minimum) and place a lighted match near the barrel top.
- Adjust the air supply so as to secure a blue flame with a well-defined inner cone.
- A yellow flame indicates incomplete combustion and will deposit soot.
- A clear blue flame indicates complete combustion and will not deposit soot.
- When gas and air are adjusted so that there will be no excess of either, the flame will appear to have a well-defined inner cone.
- The region immediately above the inner cone is the hottest part of the flame.

- The tip of the outer flame is relatively rich in oxygen and is referred to as the oxidizing flame.

Heating Liquids and Solids

The teacher and the pupils will find many occasions when heating a liquid or solid will be necessary in the chemistry course. The teacher should know the safety precautions necessary and require pupils to be familiar with correct procedures before they heat any substance in the laboratory. High school laboratory manuals usually contain the diagrams and instructions pertaining to the proper techniques for heating substances in the chemistry laboratory.

- The use of some protective device for the eyes is recommended when heating liquids.
- Never heat a test tube containing any substance (including water) while it is pointed toward you or anyone else.
- Always use a test tube holder when heating any substance in a test tube.
- Place beakers, flasks and evaporating dishes on a wire gauze to spread the heat when using a ringstand.
- Use a water bath to evaporate liquids that will catch fire easily.
- To heat a substance in a crucible, support the crucible on a clay triangle and let the flame strike the crucible directly.
- The formation of large bubbles in boiling, due to local superheating and referred to as "bumping," can sometimes be prevented by the addition of a few glass beads or small pieces of capillary tubing to the liquid.
- In situations where the temperature must be controlled with a high degree of precision, the use of drying ovens and electric heating mantles will be necessary.

A-4. The Chemical Stockroom

A well-organized system of storing chemicals and other supplies is one means of reducing the time required for laboratory chores.

Note: The following suggestions should be considered *only* if they do not conflict with local ordinances or school regulations governing the storage and handling of chemicals.

(1) **Storing Chemicals.** The chemical stockroom can be divided into three main areas for the storage of reagents. Bottles of solutions and diluted acids and bases are put together in one section. The lower shelves on all sides of the room are reserved for concentrated acid supplies and large stock bottles. Other chemicals can be placed on the remaining shelves.

Containers should be arranged in a well-defined order so that time is not wasted in hunting for a specific material. Refer to the chemical section in any scientific catalog. Note the alphabetical order in which the names of the chemicals appear. Although a metal and its compounds are grouped together, observe that the metal is listed first, then the compounds according to the alphabetical order of the anions. Use the same system to store the reagents in each section of the stockroom.

As the chemicals are placed on the shelves, arrange the bottles in rows. Place only the same material in the same row when the shelf is above eye level. Elsewhere, different reagents can be arranged in the same row providing the containers are far enough apart for their labels to be seen easily.

The section of the shelf required for the storage of a metal and its compounds should be marked off by a strip of masking tape fastened to the edge of the shelf. Using a felt pen or dark crayon write the name of the metal on the masking tape label. The same kind of label is used to mark all sections of the shelving.

(2) **Storing Glassware.** Since most of the glassware used by the pupils and teacher is kept in the demonstration or laboratory desk drawers, only the reserve supply needs to be kept in the stockroom. Keep the glass in the original cartons, but mark each box with the name and size of the contents. Place the packages in a convenient place in the stockroom. Often the top shelf is used.

Some laboratories have separate cupboards for the storage of glassware. Assign a place for each kind of glass apparatus, and then subdivide the area according to the size of the apparatus. Mark each section with masking tape labels.

(3) **Storing Other Apparatus.** Because chemical fumes can be caustic, it is best to store metallic apparatus outside of the chemical stockroom. If small drawer space is available in the laboratory, use a separate drawer for each type of apparatus. Large drawers can be partitioned off to allow like materials to be stored together. Always label the drawers.

If only shelf space is available, select boxes which just fit in between the shelves. Remove the box tops, and put each type of apparatus into a separate box. Set the labeled containers in alphabetical order on the shelves. As its contents are needed, a box can be pulled out like a drawer.

(4) **Storing Other Supplies.** Use the system described in *(3)* above for the storage of supplies such as filter paper, wooden splints, sponges and corks. Keep the different sizes of rubber stoppers and corks in separate containers.

(5) **Keeping the Stockroom Equipped.** The yearly supply order can be done easily:

- Keep a clipboard hanging in the stockroom. As a supply of a reagent falls to less than that needed for the next school year, write the chemical's name on the clipboard. Use the list for making out the supply order.
- Buy reagents in five-pound quantities where possible and where large quantities are to be used. The larger the quantity, the cheaper the rate per pound. Bulk buying reduces the length of the yearly supply order since the larger quantities will last usually for more than one year.

(6) **Dispensing Chemicals from the Stockroom.** Supplies for laboratory classes can be quickly distributed if there are as many bottles of each reagent as there are supply tables or shelves in the laboratory.

- As each chemical is unpacked, fill the required number of jars. Leave the excess material in the original container. Place all the jars on the shelf according to its alphabetical order. After use, refill each bottle before returning it to the shelf.
- Make several liters of a solution at a time. Fill the required number of bottles, and store them in the solution section of the stockroom. Excess solutions can be kept in large stock bottles on the lower shelf.
- Do not discard the empty concentrated acid bottles. Remove the labels, and wash the bottles. Use them to store other solutions or quantities of diluted acids.
- Colored plastic spoons can help prevent contamination of supply bottles resulting from the use of spoons to which other chemicals are sticking. On the laboratory blackboard list the formula for each solid to be used. After the formula put a colored square that matches the color of the plastic spoon to be used with that reagent.

Appendix B

Visual Aids

Most topics in chemistry can be visualized. Visualization is always used to good advantage by itself as well as to accompany teacher presentations. A wide variety of visual aids can contribute to the understanding of chemical principles and phenomena. These include:

- **Overhead projectors**
- **Models**
- **Teacher demonstrations**
- **Individual pupil laboratory work**
- **Films, slides and filmstrips**

B-1. The Overhead Projector

The overhead projector is proving to be of special value in chemistry instruction. Since the projector is in front of the room, the distance from the light source to the screen is only 5 to 8 feet, and the light intensity is remarkably preserved. The projector used in the laboratory should have a 10 × 10-inch stage and use 750-watt or 1,000-watt lamps. Some advantages of the overhead projector are:

- The projector will not only accept slides, but the depth of focus is also such that many physical demonstrations can be projected greatly magnified.
- In a fully lighted room the teacher works facing the class, maintaining perfect classroom contact; the pupils can take notes or copy diagrams, while blackboard work and other types of demonstration tie into a smooth running discussion without interruption of concentration.
- Ventilation of the room is undisturbed.
- Visibility is excellent even in a large room.
- All transparent materials are projected in full color, other materials in silhouette. All motion is projected. There is nothing to thread, no slide holders or moving parts of any kind. Slides are placed on the projector right side up (instead of "upside down and backwards"), and the teacher sees on the projector, without turning his head, exactly what the class sees on the screen.

- The illuminated stage of the projector makes an excellent demonstration stand even without the projection feature.
- Many ideas for using the projector have been advanced including demonstrations of acid-base indicators, reaction of metals with acids and crystallizations.

Under conditions found in many laboratories the best projector stand height is about 40 inches. This stand may be an inexpensive commercial filing cabinet mounted on a homemade dolly with casters.

Construct a permanent corner screen of inexpensive wallboard and paint it with three coats of flat white paint. This has several advantages. Located in the corner, it is not obstructed by apparatus on the demonstration table, and in turn does not obstruct the blackboard. No pupil sits behind the projector, which is in the side aisle. A beaded screen reflects a more brilliant image to those seated in front of it, but a matte surface gives an equal view to all seats in the room.

The following suggestions should aid teachers in the effective use of the overhead projector.

- **Hand-Drawn Slides.** Clear acetate sheets are inexpensive. Art supply stores carry an ink that will cling to the acetate without coalescing into droplets.
- **Diazo Process Slides.** Production of slides becomes much easier by drawing on plain paper and transferring to a slide by the diazo process (also called a "foil"). There is a paper available marked with a graph ruling that does not reproduce onto the slide; this makes a neat and square diagram easy to achieve. This paper "master" and the sheet of diazo slide are exposed to ultraviolet light (a suntan lamp) and then dry developed by exposure to ammonia fumes (a wad of absorbent cotton soaked in concentrated ammonia solution in a pickle jar). The job of drawing the paper originals may be done by pupils.
- **Photocopy Process Slides.** Photocopy machines may also be available in offices and schools, and a material is now available for making fine transparent slides. The photocopy process seems a little more expensive all around, but has the advantage of being able to make slides from an opaque material or material that is printed on both sides. The ideal situation is a combination of the two methods —diazo and photocopy.
- **Autopositive Paper Method.** This spectacular material does not require a darkroom or special light source and will make paper 'masters" from any kind of original material. It makes the very best copies of photographs.

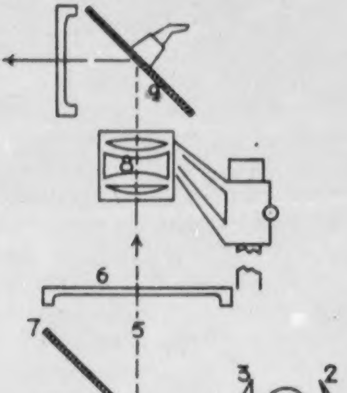
- **Photographic Process Slides.** If the teacher likes photography, or a pupil happens to be an advanced amateur, this is the only copy process in which the size of the original material can be enlarged. While something can be done with conventional amateur materials, there are cheaper and far better materials made specifically to do this job. These materials are not sold by local camera stores, but the dealers are listed as suppliers to the graphic arts or industrial photography.

Diagram *B-1a* illustrates the principle of the overhead projector.

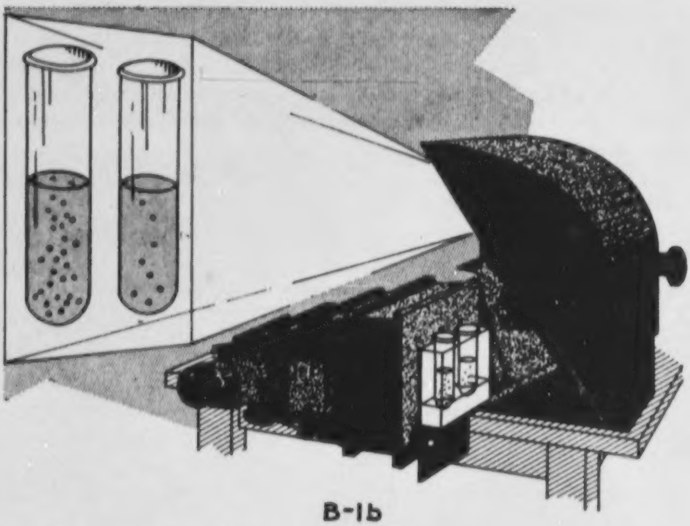
Parts and Arrangements of an Overhead Projector

1. Lamp
2. Reflector
3. Condenser lens
4. Fan
5. Path of light
6. Aperture
7. Mirror
8. Objective lens
9. Front surface mirror

The overhead projector as seen in actual operation is shown in diagram *B-1b*.



B-1a



B-1b

B-2. Atomic and Molecular Models

The creation of accurate visible models was the break-through point in modern physical science. Models are put to daily use in chemical research and are now considered to be among the basic "tools of the chemist."

The following *three* distinct classes of models are valuable:

- Atomic models used to show the arrangement of electrons about the nucleus
- Molecular scale models (snap-fastener type), principally used to illustrate the arrangement of atoms in covalent molecules
- Crystal models (peg and ball types), usually nonscalar, used to show the arrangement of atoms in ionic lattices

While the teacher is cautioned against spending excessive time of his own or that of the pupils, a certain amount of valuable instruction is gained by constructing three-dimensional models of styrofoam. Styrofoam spheres are available in various sizes and colors from Star Band Company, Broad and Commerce Streets, Portsmouth, Va.

Use black masking tape strips (1/4 in. x 1 in.) to label the electron spheres; two strips indicate the "plus" charge on a proton; no indicated charge on the neutron. Use white vinyl resin water-glue to fasten imbedded alnico magnets into the spheres, the spheres will then stick to steel chalkboard.

Use tempera paints, mixed with water (plus a drop of liquid detergent). Brush paint onto styrofoam spheres with a soft camel hair brush. Dry. Seal on color with a spray of Krylon Crystal Clear at a distance of 1 foot. (Alternate painting: Dip spheres into water emulsion latex paints. Several dips with drying between coats will give a firmer sphere than obtained with the water tempera paint.)

Atoms can be fastened together with pipe-stem cleaners, dipped into white vinyl resin water-glue.

Commercial models may be obtained from several supply houses.

B-3. Constructing a Felt Board

Although many activities can be presented by using only a blackboard, the felt board can be used to give a fresh approach to the subject. This visual aid is seldom used in high school, and its colorful display demands the immediate attention of the pupils. The speed with which it can be used and its materials changed makes the felt board an easy device to use.

An inexpensive felt board can be made from one-half yard of colored felt. Use masking tape to fasten the felt cloth to the blackboard, or staple the material to heavy cardboard, and set it on the chalk tray. In mounting the felt, be sure that the cloth is stretched out smoothly and is securely fastened.

Materials to be displayed on the felt board may be made from felt. Use a razor or scissors to cut objects from contrasting colored felt. One-fourth of a yard of each of six different colors of felt should be sufficient to make all the cutouts needed for activities using the felt board. The two felt surfaces adhere together until disturbed.

If it is desirable to add a name, symbol or formula to the felt board, a card bearing the information should be made. Use a pen and India ink or a felt marking pen to print the information on a file card or piece of cardboard. To make the card stick to the felt, paste the smooth side of strips of coarse sandpaper on the back of the card, and press the card against the felt board. The sandpaper's rough surface will adhere to the felt. The size of the sandpaper strips depends upon the size of the card to be held on the felt. A 1- x 3-inch strip can hold a 3- x 5-inch file card in position.

Felt board materials can be stored in envelopes, folders or boxes and used over a period of several years.

Note: It is important to prepare all felt board materials in advance of the class period. The effectiveness of this visual aid depends upon the speed with which the materials can be changed.

Appendix C

Planning a Field Trip

Whether the field trip is short or extended, its success as an educational experience is largely dependent upon proper planning and proper conduct on the part of the pupils. The following suggestions should prove helpful in planning a meaningful field trip.

(1) **Advance Preparation for the Trip.** Each trip should have a definite objective. For example, the objective might be to observe the work of a research chemist in a research laboratory. The teacher and pupils should work out together a list of observations to be made.

Previous to the trip, the teacher should go to the site to be visited. Plans for conducting the observations should be made on the spot. It is helpful for the teacher to make a few notes for a short talk to the pupils and to jot down additional items that might be called to the attention of pupils. Some items might include: type of equipment used, organization of the laboratory operation, types of products produced and uses of these products.

The teacher should check the preparation of the class visit carefully by verifying the time, permission and special instructions with the person in charge of the institution involved.

(2) **Preliminary Instructions.** The following points should be considered carefully:

- Purpose of trip and destination explained fully in advance of the trip
- Time of departure and return
- Appropriate clothing
- Some *specific* things to observe
- Equipment needed, particularly notebooks
- Safety precautions to be followed
- Necessity of keeping together and with the teacher and leader
- Parental permission slips
- Provision for lunch when necessary

(3) **Conducting the Trip.** The following points should be observed:

- Be sure that all comments on observations are simple and adapted to the level of the group.
- Encourage questions and be sure that all hear and understand the questions and answers.
- Repeat all important points again and again.
- Give more than facts and names; if possible, present "human interest" information about items seen.
- Make the most of unexpected occurrences and observations volunteered by the group.
- Check to make sure pupils are recording pertinent information and observations in their notebooks.
- Emphasize the relationship of principles of chemical reactions to human and/or industrial applications.
- Insist upon proper conduct.

(4) **Summary of the Trip.** The following points should be included in the summary:

- Discuss the highlights and important findings. This is best done on the spot after observations have been made and relationships pointed out.
- When space is available, pupils can be seated comfortably for an overview of the observations made on the trip.
- If necessary, the summary may be made in the classroom immediately upon returning. The important thing is that the trip should be so timed as to provide opportunity for a summary.
- For most trips oral and written reports by pupils are appropriate.

(5) **Evaluation.** Important facts and concepts relating to the field trip should be evaluated by incorporating them in examinations.

Appendix D

Preparing Reports

D-1. Using the Library

No course in chemistry should be bound by the content, views and theories expressed in a single textbook. Frequent assignments requiring the use of the library not only allow for a wider scope of the subject and a variety of viewpoints but also provide for a means of presenting up-to-date scientific chemical knowledge.

Before the library is to be used in connection with a teaching assignment, it is absolutely necessary that the teacher of science be acquainted with the resources and services of both the school and community libraries. Visit each library early in the school year.

- Meet the librarians and explain the purpose of the visit.
- Look through the 500 and 600 sections of the shelves to see what science books are available.
- Check the periodical list, and note any scientific magazines that can be used. Explore the periodical indexes such as *Reader's Guide to Periodical Literature.*
- Examine the material in the pamphlet file. It may contain useful materials for a chemistry class or the bulletin board.
- Check the procedure that should be used when materials are to be borrowed for use in a class library.
- Find out what system is to be followed when books are to be placed on reserve. Reserving books makes it possible for a large number of pupils to use the materials in a short period of time.
- Often books can be obtained for the class through a State Library or other interlibrary loan. Inquire about the procedure that is to be followed in using this service.
- Ask if the library compiles a bibliography for a specific subject area. It is helpful in planning reading assignments if a bibliography is available.
- Some libraries have films and records for circulation. Visit the audiovisual section. Find out what is available for circulation and the conditions under which they are borrowed. Obtain the library's audiovisual catalog. Other film and filmstrip catalogs are usually available. Ask to see them.

- Have the librarian show you some science books designed to fit the needs of the poor reader. Remember that a slow reader can be encouraged to enjoy a library assignment if the teacher steers him toward books he can handle.

The *first* rule of using a library is: *Know your library.*

Although it is impossible for a science teacher to read all the books in the library, he must be familiar with the literature he expects the pupils to use.

- Quickly scan the books in the area to be covered by the assignments. Numerous diagrams, mathematical treatment and technical vocabulary are the clues to the depth of the books. On the bibliography, code the books listed: 1—*easy to read,* 2—*more advanced,* 3—*very technical.* Use the information when making assignments to specific pupils.
- Set up a definite personal reading program. Include scanning new books, periodicals, abstracts and book reviews in professional magazines. Books of special interest should be studied more thoroughly.

The *second* rule of using the library in teaching is: *Keep acquainted with the literature available.*

The librarian can be of great assistance to teachers and pupils.

- In many schools a librarian can arrange to teach the class about the science section of the library. The lesson may also include the use of the card catalog, a tour of the library, borrowing procedures, the use of reserve books and reference books such as scientific dictionaries and handbooks, and periodical guides.
- Ask the librarian to give some science book reviews to the class. Often many students are inspired to read books that ordinarily they would pass by.
- Remember that a librarian is a busy person. Plan visits with her at least a week in advance. Also give advance notice concerning an assignment that will involve the use of the library. Pupils can have more help and materials when the library can plan for the science pupils in large numbers.
- Be specific in the assignments. Don't make them too general. A librarian cannot be expected to have the science teacher's store of science knowledge. However, she is trained to use library tools which supply information on definite questions. Make the assignment clear to both pupils and librarian.

The *third* rule definitely says: *Give the librarian a chance to work effectively.*

When planning assignments that will include the use of the library, remember that it is not always convenient for a pupil to get to the public library in the evening, that his schedule may not allow him to go to the school library that day and that the pupil may want to read more than has been assigned.

- Allow at least two days for a library assignment. Usually the assignment can be given several days in advance so the pupil can budget his time accordingly and plan to use the library at his convenience.
- Be sure the library has information of the assignment. Don't waste the time and effort of the pupils and the librarian.
- Plan to have some discussion on the assignment. Don't let pupils feel the library assignment is not important.
- Many teachers give extra credit for additional reading assignments. Be sure to expect the quality of the reading and the amount covered to be in keeping with the ability of the pupil.

The *fourth* rule indicates: *Library assignments require more time to prepare than the usual day-to-day ones. Plan ahead.*

D-2. Making an Assignment Requiring the Use of Reference Materials

After the pupils have become acquainted with the resources of the library, assignments requiring the use of reference materials should be encouraged. The preparation can involve the entire class, a small group or an individual pupil.

Assignment Involving the Entire Class

Sometimes it is desirable for the entire class to turn to the library for additional information on the subject under discussion.

- Make the assignment in the form of a question, such as "What additional information can be found on this topic?" Be sure the pupils know exactly what the topic is. Expect only a random sampling of the resources.
- When the topic is broad, it is wise to divide the class into groups. Make each group responsible for a definite phase of the subject.
- At times it is desirable to have specific reference materials used. Before class time prepare a bibliography card for each resource. The card should include information such as title, author, publisher and copyright date. When giving the assignment make each pupil responsible for the reference listed on the bibliography card given him.
- Another technique of giving assignments centered around specific references uses a master bibliography list. If possible, at the beginning of the year give each pupil a copy of the list. If each reference is numbered, the assignment can be quickly given since the teacher refers to the list number rather than the author or title.

After time has been allotted for the completion of the assignment, have the pupils report on their findings:

- A few pupils may give a detailed summary of their readings. Additional facts may be contributed by the rest of the class.
- Each pupil may contribute one or two items gleaned from his reading.
- A team may compile one report which is either read by one of the team members or is duplicated and a copy given to each pupil.
- A panel made of one member from each team may discuss the assignment. Questions coming from the class are referred to the appropriate team for answers.

The Group Assignment

When the amount of reference material is limited, it is wise to ask only a small group of pupils to use the material. Employ the same techniques listed for class assignments.

The Pupil Assignment

Usually the individual assignment comes on the spur of the moment:

- A pupil is asked to look up something in a dictionary or handbook. The information is given to the class within a few minutes.
- Someone wants to know something not of general interest or in the realm of subject matter being discussed. The teacher refers the pupil to a specific reference(s) for obtaining the answer.
- When a question is raised relative to the subject under discussion and the teacher does not feel he should answer the question, the pupil is referred to a resource. Again it is wise to steer the pupil toward the best references.
- A question sometimes comes up, and the teacher does not know the answer. Do not hesitate to admit a lack of knowledge. Give the library assignment to the pupil, but also include a statement that the teacher will look up the answer, too. Make the class report a pupil-teacher one.

D-3. Writing a "Research" Report

Pupils should be assisted by the teacher in receiving information relative to the correct procedure for drafting a "research" report. This will not only assist the pupils to learn the correct method but prevent them from wasting time upon incorrect and time-consuming processes. Discuss such points as the ones listed below:

- The title should be descriptive and specific.
- The report must show evidence of organization.

- A short abstract of the contents and conclusions precedes the body of the report to provide the reader with a quick survey.
- The body of the report follows an outline that insures that all points will be covered and that the writing is kept on target.
- The content is factual, objective and easily read.
- The correct word is used. Knowledge of language is evident, and the spelling is flawless.
- All conclusions and recommendations are supported by evidence of quotation.
- The scientific apparatus is accurately described, and the working details of experiments are complete.
- Illustrations, such as diagrams, curves, photographs, charts and tables, are used freely.
- The work of other scientists is always given credit.
- Footnotes and references are provided.
- The most important discovery is not a contribution to science until it has been communicated to others.

The standard form for an outline should be used.

I. ________________________________
    A. ______________________________
        1. ____________________________
        2. ____________________________
            a. __________________________
            b. __________________________
    B. ______________________________
II. ________________________________

Appendix E

Mathematics Used in Chemistry

E-1. Significant Figures

Any measurement is by necessity only an approximation because there is no measuring device which is absolutely perfect. If the weight of an object is given as 20.3 grams, this indicates that the weight of the mass was determined accurately to the nearest tenth gram; 20.30 grams indicates weight to the nearest hundredth gram; 20.300 grams to the nearest thousandth gram, and so on. The number 20.3 contains 3 significant figures (2, 0 and 3), 20.30 contains 4 significant figures (2, 0, 3 and 0).

A significant figure is one which is known to be reasonably reliable. Zeros which appear in *front* of a number are *not* usually significant figures but those which appear *after* a number are significant figures. For example:

0.083 — 2 significant figures
430 — 3 significant figures
0.006158 — 4 significant figures
7.006158 — 7 significant figures
16,800 — 5 significant figures

The following rules will assist pupils when rounding off a number:

- When the number dropped is less than 5, the preceding number remains unchanged. For example, 5.3634 becomes 5.363.
- When the number dropped is more than 5, 1 is added to the preceding number. For example, 2.4158 becomes 2.416.
- When the number dropped is exactly 5, if the preceding number is even, it remains unchanged; if the preceding number is odd, 1 is added. For example, 3.745 becomes 3.74 while 5.375 becomes 5.38.
- When adding or subtracting, the answer should be rounded off so as to contain the least accurately known figure as the final one. For example,

Add		Subtract	
32.6			
431.33		531.46	
6144.212		86.3	
6608.142	= **6608.1**	445.16	= **445.2**

- **When multiplying or dividing, the answer should be rounded off so as to contain only as many significant figures as are contained in the least accurate number. For example,**

Multiply	Divide
1.36	5.1 ÷ 2.13
4.2	2.39 = **2.4**
272	$2.13\overline{)5.1000}$
544	426
5.712 = **5.7**	840
	639
	2010

E-2. Powers of Ten

Very large and very small numbers should be expressed in exponential form. These large and small numbers are expressed as 10 raised to a given power.

A *power* (exponent) indicates how many times a number is repeated as a factor. For example, 10 x 10, which is 10 repeated as a factor twice, is $100 = 10^2$.

Any number raised to the zero power equals 1 ($10^0 = 1$). A number with a negative exponent is the reciprocal of that number with a positive exponent, for example, $10^{-3} = \frac{1}{10^3} = \frac{1}{1{,}000} = 0.001$

The following table illustrates the use of powers of ten:

$100{,}000 = 10^5$
$10{,}000 = 10^4$
$1{,}000 = 10^3$
$100 = 10^2$
$10 = 10^1$
$1 = 10^0$
$0.1 = 10^{-1}$
$0.01 = 10^{-2}$
$0.001 = 10^{-3}$
$0.0001 = 10^{-4}$
$0.00001 = 10^{-5}$

The following rules will assist pupils when working with powers of ten.

- **Adding and subtracting exponents.** Exponential numbers may be added or subtracted if the powers of 10 are the same. For example, $5 \times 10^3 + 2 \times 10^3 = (5 + 2) \times 10^3 = 7 \times 10^3$. If the numbers to be added have different powers of 10, then the powers must be equalized. For example, $2 \times 10^2 + 3 \times 10^3 = 2 \times 10^2 + 30 \times 10^2 = 32 \times 10^2$ or 3.2×10^3.
- **Multiplying exponents.** Exponential numbers may be multiplied by adding the exponents. For example, $10^3 \times 10^5 = 10^8$.
- **Dividing exponents.** Exponential numbers may be divided by subtracting the exponents. For example, $10^5 \div 10^2 = 10^3$.

E-3. Metric System Units

Prefix

micro — one-millionth — $\frac{1}{10^6}$ or 10^{-6}

milli — one-thousandth — $\frac{1}{10^3}$ or 10^{-3}

centi—one-hundredth— $\frac{1}{10^2}$ or 10^{-2}

kilo — one thousand — 1,000 or 10^3

UNITS	ABBREVIATION	ENGLISH EQUIVALENT
1 kilometer (1,000 meters)	km.	0.621 mile
1 meter (100 centimeters)	m.	39.4 inches
1 centimeter (10 millimeters, mm.)	cm.	0.394 inches
1 kilogram (1,000 grams)	kg.	2.20 pounds
1 gram (1,000 milligrams, mg.)	gm.	0.0353 ounce
1 liter (1,000 milliliters, ml.)	l.	1.06 quarts
1 milliliter (1.000027 cubic centimeters, cc.)	ml.	———
1 atomic mass unit (1.66×10^{-24} gm.)	a.m.u.	———
1 angstrom (1×10^{-8} cm.)	Å	———
1 electron volt (23.1 kilocalories per mole)	e.v.	———
1 erg (2.39×10^{-11} kilocalories)	erg	———
Avogadro number (6.0235×10^{23})	———	———

Appendix F

Periodicals

The following periodicals are extremely valuable as sources of reference materials for the teachers and pupils of chemistry.

Journal of Chemical Education. American Chemical Society, 500 Fifth Avenue, New York 36. Monthly. $4

Published for both college and high school teachers. The inclusion of college-level articles provides high schools with excellent enrichment materials.

Copies of the *Journal of Chemical Education* are available on interlibrary loan from the New York State Library in Albany. Such loans should be arranged through the local public library. The following is a list of libraries that carry all or part of the back issues of the journal.

Boyce Thompson Institute Library, Yonkers
Chemists Club, New York
City College of New York Library, New York
Colgate University Library, Hamilton
Columbia University Library, New York
Cooper Union Library, New York
Cornell University Library, Ithaca
Eastman Kodak Research Library, Rochester
Engineering Society Library, New York
Fordham University Library, New York
Grosvenor Library, Buffalo
Hamilton College Library, Clinton
New York State Library, Albany
New York University Library, University Heights
New York University Library, Washington Square
Pratt Institute Library, Brooklyn
Public Library, Brooklyn
Public Library, New York
Public Library, Queens
Public Library, Rochester
Rensselaer Polytechnic Institute Library, Troy
St. John's University Library, Brooklyn
St. Lawrence University Library, Canton
Skidmore College Library, Saratoga Springs
Syracuse University Library, Syracuse
Teachers College Library, Columbia University, New York
Union College Library, Schenectady
University of Buffalo Library, Buffalo
University of Rochester Library, Rochester
Vassar College Library, Poughkeepsie
Wells College Library, Aurora

Chemical and Engineering News. American Chemical Society, 1155 16th St., N.W., Washington 6, D.C. Weekly. $6

Excellent source of information on the latest in research and applied chemistry.

The following periodicals contain interesting material on several of the sciences and are suggested as possible instructional aids for all teachers and pupils of science.

Scientific American. 1415 Madison Ave., New York 17. Monthly. $5

Includes book reviews, illustrations, trade literature, chemical abstracts, engineering abstracts and psychological abstracts.

The Science Teacher. National Science Teachers Association, 1201 Sixteenth St., N.W., Washington 6, D.C. 8 times a year. Nonmembers 50¢ per month.

Includes bibliographies, book reviews, charts, illustrations and educational index.

Science Information News. National Science Foundation. Supt. of Documents, Washington 25, D.C. Bimonthly. $1.25

Bibliographies of science materials.

Science. (A.A.A.S.) 1515 Massachusetts Ave., N.W., Washington 5, D.C. Weekly. $8.50

Includes biological abstracts, chemical abstracts, engineering index, mathematical reviews, nutrition abstracts, psychological abstracts and science abstracts.

Science News Letter. Science Service Inc., 1719 N. St., N.W., Washington 6, D.C. Weekly. $5.50

A weekly summary of current science.

Science World. Scholastic Magazines, Inc., 33 W. 42d St., New York 36. Biweekly. $1.50

Contains articles of general interest on current aspects of science.

Appendix G

Radioactive Isotopes

G-1. Radioactive Isotopes for Sale under a General AEC License

ISOTOPE	USUAL CHEMICAL FORM	HALF-LIFE
Iodine 131	NaI	8.08 days
Phosphorus 32	NaH_2PO_4	14.3 days
Calcium 45	$CaCl_2$	163 days
Carbon 14	Na_2CO_3	5,568 yrs.
(Cesium 137 and	CsCl	30 yrs.
Barium 137)	$BaCl_2$	2.6 min.
Chlorine 36	KCl	308,000 yrs.
Chromium 51	$CrCl_3$	27.8 days
Cobalt 60	$CoCl_2$	5.27 yrs.
Iron 59	$FeCl_3$	45.1 days
Nickel 63	$NiCl_2$	85 yrs.
Ruthenium 106	$RuCl_3$	1.0 yrs.
Rhodium 106	$RhCl_3$	30 sec.
Sodium 22	NaCl	2.6 yrs.
Strontium 89	$SeCl_2$	53 days
(Strontium 90 and	$SrCl_2$	25 yrs.
Yttrium 90)	YCl_3	2.54 days
Sulfur 35	H_2SO_4	87.1 days
Thallium 204	$TlNO_3$	4.0 yrs.
Yttrium 90	YCl_3	2.54 days
Zinc 65	$ZnCl_2$	250 days

G-2. Application-Exempt Quantities of Radioisotopes Can Be Secured from the Following:

(1) Nuclear Consultants, Inc.
33-61 Crescent Street
Long Island City 6

(2) Abbott Laboratories
Oak Ridge Division
Oak Ridge, Tenn.

(3) Nuclear-Chicago Corporation
223 West Erie Street
Chicago 10, Ill.
(carbon 14 compounds)

(4) Isotopes Specialities Company, Inc.
170 West Providencia Street
Burbank, Calif.

(5) Atomic Research Laboratory
10717 Venice Boulevard
Los Angeles 34, Calif.

Appendix H

Equipment and Supplies

The following equipment and supplies will be needed in order to carry out the activities contained in the *Chemistry Handbook.*

No attempt has been made to indicate quantities in view of the fact that school situations vary as to whether a particular activity is teacher demonstrated, individually performed or carried out in small groups.

Schools that are unable to obtain all the necessary materials at one time should work out a systematic plan for yearly purchases over a given period of time until their chemistry laboratories are complete. Once this has been achieved, it is important to provide for replacements each year in order to keep the laboratory in an efficient operating condition.

Equipment

- Arc light
- Asbestos pads
- Atomizer
- Balance (beam, analytical, spring)
- Battery
- Battery jar
- Beakers [illegible]l-form, low-form, various sizes)
- Bearings
- Bell (electric)
- Bell jar
- Blowpipe
- Bottles (collecting)
- Brownian movement apparatus
- Bunsen burner
- Burette
- Buzzer (electric)
- Chart (periodic table)
- Chart (relative size of atoms and ions in the periodic table)
- Clamps (alligator, burette, beaker, hose, test tube)
- Cobalt glass
- Colorimeter (DuBosq)
- Conductivity of solution apparatus
- Connections (plastic, rubber)
- Cork borer
- Cover glass
- Crucible and cover (porcelain, clay, platinum, vycor)
- Cup (clay)
- Diffraction grating
- Drying tube
- Electric "blender"
- Electric heater
- Electrolysis apparatus (student form)
- Electroscope
- Erlenmeyer flask
- Evaporating dish
- Film holder
- File (triangular)
- Filter pump (aspirator type)
- Filtering flask
- Flashlight
- Florence flask
- Forceps
- Funnel (short stem, long stem, dropping, separatory)
- Geiger counter
- Glass chimney
- Glass square
- Goggles
- Graduate (graduated cylinder, various sizes)
- Hammer (claw)
- Hoffman apparatus
- Hydrometer (heavy-liquid, light-liquid)
- Iceland spar
- Induction coil
- Kipp generator

Knife (paring)
Lamp socket (porcelain)
Magnets
Marbles
Medicine dropper
Metric ruler
Microscope (compound)
Mineral collection
Mortar and pestle
Nessler's tubes
Oven
Overhead projector
Pegboard (masonite)
Petri dish
***pH* meter**
Pie tin
Pliers (long nose)
Pinchcocks
Pipette
Pneumatic trough
Power supply (a.c., d.c.—low voltage)
Pycnometer
Reflector (photographic)
Retort
Rheostat
Ringstand
Rod (stirring)
Saw (wood)
Screwdriver
Spatula
Spectrum tube (H_2, N_2, Hg)
Spoon (deflagrating)
Spoon (plastic or bone)
Stopper (rubber, various sizes)
Switch (single and double pole, single and double throw)
Test tube
Test tube brush
Test tube holder
Test tube rack
Thermometer (C., F.)
Thistle tube
Tongs
Triangle (pipestem)
Tripod
U-tube
Ultraviolet light source
Vacuum pump
Voltmeter
Volumetric flask
Watchglass
Water bath
Wing top

Supplies

Acetate paper (clear, colored)
Acetic acid (glacial, dilute)
Acetic anhydride
Acetone
Acetylene tetrabromide
Agar
Alizarin yellow
Alpha source
Aluminum chloride
Aluminum foil
Aluminum oxide *(alumina)*
Aluminum (pellets, powder, sheets)
Aluminum potassium sulfate *(alum)*
Aluminum sulfate
Ammonia (in water)
Ammonium chloride
Ammonium dichromate
Ammonium hydroxide
Ammonium phosphate
Amyl acetate
Antimony (powder)
Antimonyl potassium tartrate
Arsenic
Arsenious oxide
Asbestos fibers
Asphalt
Barium carbonate
Barium chloride
Barium hydroxide
Barium nitrate
Barium peroxide
Barium sulfate
Benedict's solution
Benzene
Bismuth
Boric acid
Brick (tap hole)
Bromine
Brom thymol blue
Brush (paint, 1 inch)
Bulb (argon, neon)
Butyl alcohol *(butanol)*
Butyric acid
Cadmium
Cadmium carbonate
Calcium
Calcium acetate
Calcium carbide
Calcium carbonate
Calcium chromate
Calcium fluoride
Calcium hydroxide
Calcium hypochlorite
Calcium nitrate
Calcium oxide
Calcium sulfate
Camphor
Candles (wax)
Carbon
Carbon disulfide
Carbon tetrachloride
Casein
Cellophane (colorless, various colors)
Chalk (various colors)
Charcoal
Chloroform

Chrome alum
Chromium oxide
Cinnabar ore
Citric acid
Cobalt chloride
Cobalt nitrate
Congo red
Copper metal
Copper carbonate
Copper nitrate
Copper sulfate
Copper sulfide
Copper wire (various gauges)
Corks (various sizes)
Cornstarch
Cotton
Cottonseed oil
Cupric bromide (anhydrous)
Cupric chloride (anhydrous)
Cupric oxide
Cupric sulfate
Detergent (liquid)
Dextrin
Diphenylamine
Dry cell
Ether
Ethyl acetate
Ethyl alcohol *(ethanol)*
Ethylene dichloride
Ethylene glycol
Fehling's solution
Felt (various colors)
Ferric chloride
Ferric hydroxide
Ferric oxide
Ferric sulfate
Ferrous ammonium sulfate
Ferrous sulfate
Film (X-ray)
Filter paper (sheets, Whatman)
Formaldehyde
Fructose
Galena (ore)
Gallium
Gases in cylinders (NH_3, CO_2, Cl_2, H_2, H_2S, O_2, SO_2)
Gelatin
Glass tubing (various diam.)
Glucose
Glycerine *(glycerol)*
Gold chloride
Gold foil
Graph paper (regular, semilog)
Graphite
Graphite electrodes
Halite *(rock salt)*
Hexamethylenediamine
Hydrion paper
Hydrochloric acid
Hydrofluoric acid
Hydrogen peroxide
Indigo blue
Indophenol
Ink (India)
Iodine crystals
Iron filings
Isopropyl alcohol
Junket (tablets)
Kerosene
Lacquer
Lactic acid
Lactose
Lampblack
Lamps (various sizes)
Lead (chunks, sheets)
Lead acetate
Lead carbonate
Lead chloride
Lead nitrate
Lead oxide
Lead sulfide
Linseed oil
Lithium
Lithium chloride
Litmus
Litmus paper (red, blue)
Lycopodium powder
Magenta
Magnesium oxide
Magnesium (ribbon, turnings, powder)
Magnesium sulfate
Magnetite (ore)
Maltose
Manganese dioxide
Marble chips
Marbles (various sizes)
Mercuric bromide
Mercuric chloride
Mercuric iodide
Mercurous chloride
Mercurous nitrate
Mercurous sulfide
Mercury
Methyl alcohol *(methanol)*
Methyl orange
Methyl oxalate
Methyl red
Methyl violet
Methylene blue
Methylene iodide
Mineral oil
Modeling clay
Molasses
Nails (various sizes)
N-amyl alcohol
Naphthalene
Nichrome wire
Nickel ammonium sulfate
Nickel nitrate
Nickel sulfate
Nitric acid
Nitropropane
Nylon powder
Oakwood
Oil red
Oleic acid

Oxalic acid
Paper toweling
Paraffin
Pegs (colored)
Pentane
Pentyl alcohol *(pentanol)*
pH paper
Phenol
Phenolphthalein
Phosphorus (red, white, yellow)
Phthalic anhydride
Plaster of paris
Platinum wire
Plumber's litharge
Potassium
Potassium bromide
Potassium carbonate
Potassium chlorate
Potassium chromate
Potassium dichromate
Potassium ferricyanide
Potassium ferrocyanide
Potassium hydroxide
Potassium iodate
Potassium iodide
Potassium nitrate
Potassium permanganate
Potassium phosphate
Potassium thiocyanate
Propyl alcohol *(propanol)*
Propylene glycol
Pyrex glass wool
Pyrogallic acid
Radioactive ores
Radioisotopes (see appendix *G*)
Razor blades
Rosin
Rubber tubing (various sizes)
Salicylic acid
Sand
Sandpaper (various nos.)
Sebacyl chloride
Sequins
Silica
Silver acetate
Silver nitrate
Silver oxide
Soap (liquid, powder, bar)
Sodium
Sodium acetate
Sodium bicarbonate
Sodium bisulfite
Sodium borate *(borax)*
Sodium bromide
Sodium calcium hydroxide *(soda lime)*
Sodium carbonate
Sodium chloride
Sodium chromate
Sodium hydroxide
Sodium iodide
Sodium nitrate
Sodium oleate
Sodium peroxide
Sodium potassium tartrate *(Rochelle salt)*
Sodium silicate
Sodium sulfate
Sodium sulfite
Sodium thiosulfate *(hypo)*
Splints (wood)
Sponge
Stannous chloride
Starch
Stearic acid
Steel wool
Straws (soda, plastic)
Strontium
Strontium nitrate
Styrofoam (blocks, spheres)
Succinic acid
Sucrose
Sugar
Sulfur (flowers, roll)
Sulfuric acid
Tacks
Tannic acid
Tape (adhesive, masking)
Taper
Tartaric acid
Thermite mixture
Thioacetamide
Thymolphthalein
Tin
Titanium tetrachloride
Toluene
Triethanolamine
Tumeric paper
Turpentine
Vaseline
Wire gauze
Xylene
Zeolite
Zinc (mossy, strips)
Zinc carbonate
Zinc chloride
Zinc sulfate

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A bibliography of chemistry projects and demonstrations. Journal of Chemical Education, v. 27, No. 10: 562-564. Oct. 1950

A home reference library for chemistry students. Journal of Chemical Education, v. 30, No. 10: 507-509. Oct. 1953

A new type of crystal model. Journal of Chemical Education, v. 34, No. 5: 220-223. May 1957

Choosing a chemical keyboard for your typewriter. Journal of Chemical Education, v. 35, No. 9: 467. Sept. 1958

Construction of crystal models from styrofoam spheres. Journal of Chemical Education, v. 34, No. 2: 99-101. Feb. 1957

Design that report. Journal of Chemical Education, v. 28, No. 10: 519-520. Oct. 1951

Molecular models for lecture demonstrations (styrofoam types). Journal of Chemical Education, v. 30, No. 10: 503-507. Oct. 1950

Projection demonstrations. Journal of Chemical Education, v. 33, No. 12: A541. Dec. 1956

Some demonstrations with the overhead projector. Journal of Chemical Education, v. 35, No. 1: 36-37. Jan. 1958

The purpose and character of laboratory instruction. Journal of Chemical Education, v. 32, No. 5: 264-266. May 1955

Writing oxidation-reduction equations. Journal of Chemical Education, v. 36, No. 5: 215-218. May 1959

Additional General References

Bibliography

The following list of books and pamphlets represents only a very limited number of the many excellent publications available. These suggestions are given in the hope that they will provide teachers with additional information which may be used to stimulate better teaching. A number of books are published each year which are valuable from the standpoint of presenting new developments in chemistry. It is highly desirable to keep a bibliography in chemistry up to date.

Alyea, H. N. & Dutton, F. B. Tested demonstrations in chemistry. Journal of Chemical Education, Easton, Pa.

Asimov, Isaac. Inside the atom. Abelard-Schuman

Castka, J. F. Chemistry problems. Holt

Clark, G. L. & Hawley, G. G., ***eds.*** Encyclopedia of chemistry. Reinhold

Curtman, L. J. & Edmonds, S. M. Calculations of qualitative analysis. Macmillan

Dearden, John. Iron and steel today. Oxford

Estok, G. K. Organic chemistry: a short text. Saunders

Everhart, J. L. Titanium and titanium alloys. Reinhold

Friend, J. A. N. Man and the chemical elements: from stone-age hearth to the cyclotron. Scribner

Gilreath, E. S. Fundamental concepts of inorganic chemistry. McGraw

Glasstone, Samuel. Sourcebook on atomic energy. Van Nostrand

Gould, E. S. Inorganic reactions and structure. Holt

Hayward, C. R. Outline of metallurgical practice. Van Nostrand

Hoffman, Banesh. Strange story of the quantum. Dover

Johnson, C. G. Metallurgy; 4th ed. Am. Tech. Soc.

Kendall, James. Great discoveries by young chemists. Crowell

Keyser, C. A. Basic engineering metallurgy. Prentice-Hall

Manufacturing Chemists' Association, Incorporated. Guide for safety in the chemical laboratory. Van Nostrand

———— Scientific experiments in chemistry. Holt

Miner, H. A. & others, *eds.* Teaching with radioisotopes. United States Atomic Energy Commission, for sale by Govt. Ptg. Office

Morris, J. L. Modern manufacturing processes. Prentice-Hall

Nebergall, W. H. & Schmidt, F. C. College chemistry. Heath

Newton, Joseph. Extractive metallurgy. Wiley

Pauling, L. C. College chemistry. Freeman
———— General chemistry; 2d ed. Freeman
———— The nature of the chemical bond and the structure of molecules and crystals; an introduction to modern structural chemistry; 3d ed. Cornell Univ. Press

Purdy, G. A. Petroleum: prehistoric to petrochemicals. McGraw

Quagliano, J. V. Chemistry. Prentice-Hall

Reinfeld, Fred. Uranium and other miracle metals. Sterling

Sax, N. I. Handbook of dangerous materials. Reinhold

Schenberg, Samuel, *ed.* Laboratory experiments with radioisotopes for high school science demonstrations. United States Atomic Energy Commission, for sale by Govt. Ptg. Office

Sienko, M. J. & Plane, R. A. Chemistry. McGraw

Sorum, C. H. How to solve general chemistry problems. Prentice-Hall

Syrkin, Y. K. & Dyatkina, M. E. Structure of molecules and chemical bond. Butterworths Scientific Publications, London

Weeks, M. E. Discovery of the elements; 6th ed. Journal of Chemical Education, Easton, Pa.

Wilkinson, W. D. & Murphy, W. F. Nuclear reactor metallurgy. Van Nostrand

Woodburn, J. W. Nuclear science teaching aids and activities. Office of Civil and Defense Mobilization, Battle Creek, Mich.

Additional Bibliography Entries

This booklet is published primarily for use in the schools of New York State, and free copies are available to New York State school personnel when ordered through a school administrator. Residents of New York State may buy copies at $1.50 each from the Publications Distribution Unit, Room 169, Education Building, Albany N.Y. Remittances should be made payable to the New York State Education Department.

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